AI-68-104

PB 179908

DEVELOPMENT OF A MOLTEN CARBONATE PROCESS FOR REMOVAL OF SULFUR DIOXIDE FROM POWER PLANT STACK GASES

SUMMARY REPORT

JUNE 1, 1967 TO FEBRUARY 28, 1968

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va. 22151

AI-68-104

DEVELOPMENT OF A MOLTEN CARBONATE PROCESS FOR REMOVAL OF SULFUR DIOXIDE FROM POWER PLANT STACK GASES*

SUMMARY REPORT

June 1, 1967 to February 28, 1968

The work upon which this publication is based was performed by Atomics International, a Division of North American Rockwell Corporation, Canoga Park, California, pursuant to Contract No. PH 86-67-128 with the U.S. Public Health Service, Department of Health, Education, and Welfare.

---

*The basic process is a proprietary development of North American Rockwell Corporation

CONTENTS

Page

Summary 1

I. Introduction 5

A. The Process Concept 5

1. Flow Diagram 5

2. Process Chemistry 5

3. Special Features 10

B. The Development Program 11

1. Development Requirements 11

2. Initial Development Program 12

II. Results 13

A. Process Chemistry 13

1. Analytical Methods 14

2. Absorption Studies 15

3. Reduction Studies 23

a. Carbon Reduction Tests 24

b. Rotating Packed Bed Contactor Tests 24

c. Catalyzed Reduction Tests 56

4. Regeneration Studies 72

a. Regeneration of Synthetic Melts 74

b. Regeneration of Melts from Reduction Tests . . 80

5. Cycle Tests 94

6. Regeneration Equilibrium Studies 98

B. Corrosion Studies 102

1. The Test Program 102

CONTENTS (Cont.)

Page

2. Screening Tests 103
   a. Tests at 930°F 103
   b. Tests at 1110°F 108
   c. Tests at 1290°F 111
3. Long-Term Tests 113
   a. Tests of Type 347 Stainless Steel at 950°F 114
   b. Tests of Type 347 Stainless Steel at 1100°F and 1300°F 117
4. Future Work 119

C. Contactor Development 119
1. Scrubber Contactor Development 120
   a. The Test Stand 120
   b. Wetted-Wall Contactor Tests 122
   c. Baffled-Tube Contactor Tests 125
   d. Nitric Oxide Effects 128
   e. Spray Tower Tests 131
2. Reducer Contactor Development 132

D. Component Development 132

E. Pilot Plant and Component Test Loop Design 134

III. Present Status 138

A. Process Chemistry 138

B. Corrosion Studies 139

CONTENTS (Cont.)

Page

C. Contactor Development 140

D. Component Development 141

E. Pilot Plant and Component Test Loop Design 141

IV. The Reference Process 141

V. References 144

Appendix A. Analytical Procedures 145

Appendix B. Fly Ash Compositions 149

Appendix C. Alloy Compositions 150

Appendix D. Nomenclature 151

Appendix E. Thermodynamics 152

TABLES

Page

1. Properties of Carbonate Melt at 800°F (427°C) 7
2. Absorption Test Conditions 16
3. Absorption Test Melt Sample Compositions 18
4. Experimental Conditions - Hydrogen Reductions at 1110°F (600°C), 1 atm 27
5. First Test - Hydrogen Reduction of Sulfate at 1110°F (600°C) . . 28
6. Second Test - Hydrogen Reduction of Sulfite at 1110°F (600°C) 30
7. Third Test - Hydrogen Reduction of Sulfite at 1110°F (600°C) 31
8. Hydrogen Reduction of Sulfate at 980°F (525°C) 33
9. Hydrogen Reduction of Sulfate at 1290°F (700°C) 34
10. Half-Life Values of Hydrogen Reduction Reactions 38
11. Test Conditions, Hydrogen Reduction with Graphite Packing 40
12. Test Results, Hydrogen Reduction with Graphite Packing at 1110°F 40
13. Iron Content of Melt Samples 45
14. Experimental Conditions, CO Reduction Tests 46
15. First Test - Carbon Monoxide Reduction of Sulfate at 1170°F (630°C) 47
16. Second Test - Carbon Monoxide Reduction of Sulfate at 1170°F (630°C) 49
17. Typical Producer Gas Composition 51

TABLES (Cont.)

Page

18. Experimental Conditions, CO-H_2 Reduction Tests 51
19. First Test - Reduction of Sulfate with CO-H_2 Mixture at 1170°F (630°C) 52
20. Second Test - Reduction of Sulfate with CO-H_2 Mixture at 1170°F (630°C) 53
21. Catalysts Studied with Hydrogen at 1110°F (600°C) 57
22. Results of Control Test with Hydrogen at 1110°F 59
23. Results of Iron Catalyst Tests at 1110°F 62
24. Results of Tin Catalyst Test at 1110°F (600°C) 64
25. Free Energies of Reactions 15 and 16 67
26. Results of Tests at 1200°F (650°C) and 1290°F (700°C) 69
27. Average Reduction Rates 71
28. Results of Carbon Monoxide Reduction at 1290°F (700°C) 72
29. Regeneration Test Conditions 82
30. Melt Composition During Regeneration 83
31. Sulfur Balances 84
32. Results of Cycle Test in Graphite System 96
33. Free Energy and Equilibrium Constants for the Sodium Regeneration Reaction 98
34. Hydrogen Sulfide Absorption Test Conditions 99
35. Hydrogen Sulfide Absorption Test Results 99
36. Comparison of Equilibrium Constants 100
37. Materials Given Corrosion Screening Tests at 930°F 104
38. Materials Warranting Further Testing 105

TABLES (Cont.)

Page

39. Corrosion of Metals in Molten Salts 106

40. Materials Given Corrosion Screening Tests at 1110°F 108

41. Corrosion of Metals in Molten Salts at 1110°F 109

42. Corrosion of Metals in Molten Salts at 1290°F 112

43. Test Conditions, Type 347 Long-Term Test at 950°F 114

44. Corrosion of Type 347 Stainless Steel at 950°F 115

45. Wetted Wall Contactor Test Conditions 122

46. One Inch Diameter Wetted Wall Contactor Test Results . . . 123

47. Baffled-Tube Contactor Test Results 127

48. Baffled-Tube Contactor Test Results with Nitric Oxide . . . 130

49. Fly Ash Filtration Test Results 133

FIGURES

Page

1. Basic Process Flow Diagram 6
2. Absorption Test Apparatus 17
3. Conversion of Sulfite to Sulfate 20
4. Absorption Test Schematic 22
5. Rotating Packed Bed Contactor 26
6. Reduction of Sulfate with Hydrogen 29
7. Reduction of Sulfate-Sulfite with Hydrogen 32
8. Sulfate Reduction with Hydrogen at 980°F (525°C) 35
9. Sulfate Reduction with Hydrogen at 1290°F (700°C) 37
10. Arrhenius Plot 39
11. Reduction of Sulfate with Hydrogen in Graphite-Packed Contactor at 1110°F (600°C) 41
12. Comparison of Results of Reduction Tests at 1110°F (600°C) . . 43
13. Iron Content of Melt Samples 44
14. Reduction of Sulfate with Carbon Monoxide 48
15. Reduction of Sulfate with $CO-H_2$ Mixture 54
16. Uncatalyzed (Control) Reduction Test at 1110°F (600°C) . . . 58
17. Iron Catalyst Test Results 61
18. Comparison of Tin and Iron Catalysts 65
19. Effect of Temperature on Reduction Time 70
20. Carbon Monoxide and Hydrogen Reductions at 1290°F (700°C) . . 73
21. Rotating Reactor for Carbonate Regeneration 75
22. Bubbler Reactor for Carbonate Regeneration 78

FIGURES (Cont.)

Page

23. Regeneration of Melt R1 85

24. Regeneration of Melt R2 86

25. Regeneration of Melt R3 87

26. Regeneration of Melt R4 88

27. Regeneration of Melt R5 89

28. Regeneration of Melt R6 90

29. Regeneration of Melt R7 91

30. Contactor Test Stand 121

31. Baffled-Tube Contactor 126

32. Pilot Plant Flow Diagram 135

33. Component Test Loop Flow Diagram 137

34. Reference Process Flow Diagram 142

SUMMARY

Atomics International is developing a molten carbonate process to remove sulfur oxides from power plant stack gases, under contract PH 86-67-128. In this process, the sulfur oxides are absorbed in a molten mixture of lithium, sodium, and potassium carbonates. The resulting carbonate-sulfite mixture is then regenerated chemically. Work began June 1, 1967, with effort in four major areas: process chemistry, corrosion studies, contactor development and component development. Since then, work has also been initiated on pilot plant and component test loop design. The results achieved through February 28, 1968, are summarized below:

A. PROCESS CHEMISTRY

1. Absorption

The absorption tests showed that the absorption reaction was very rapid and that oxygen, water vapor, and fly ash would not interfere with removal of the sulfur oxides by the molten carbonate. It was also found that some of the sulfite formed was oxidized to sulfate, the amount depending on contact time and oxygen content of the flue gas. Tests with combustion gases showed that large amounts of excess oxygen would oxidize sulfide and sulfite in the melt to sulfate, and that hydrogen sulfide would not be emitted from the melt even when sulfides were contacted with moist flue gases. The tests thus showed that the carbonate melt was an excellent absorbent under realistic conditions, with a very fast reaction rate. The main problem involved in the absorption process is to bring the sulfur oxides into good contact with the carbonate melt.

2. Reduction

Satisfactory reduction tests were performed using hydrogen at 1100°F and a hydrogen-carbon monoxide mixture at 1170°F, and essentially

---

The basic process is a proprietary development of North American Rockwell Corporation complete reductions of typical process melts were obtained in 60 and 80 minutes, respectively.

Recent reduction studies have concentrated on catalysis. Iron and tin compounds have been found to increase the rate of the reduction reaction, and a reduction reaction mechanism has been proposed which may lead to other catalysts. Reduction rates under process conditions will have to be determined in tests combining catalysis with optimum gas-liquid mass transfer. However, it is expected that the results of preliminary tests, indicating 1 hour would be required at 1100°F, may be improved upon somewhat.

3. Regeneration

Regeneration tests have shown that the melts can be regenerated to carbonate for recycling to the scrubber, and that the sulfur can be recovered as hydrogen sulfide with good efficiency. However, there are indications that the reduction catalysts cause foaming problems during regeneration, and also tie up some of the sulfur. The foaming may be eliminated by carrying out the regeneration reaction in large surface area reactors, and the sulfur tie-up may not occur after the catalyst is saturated. Further studies, including cycle tests, will be performed to study these effects.

B. CORROSION STUDIES

Screening tests have been completed for most practical metals and alloys, and certain candidates have been selected for long-term tests. Long-term tests of type 347 stainless steel have shown it to be suitable for use at 950°F with any melt, but unsuitable with melts containing sulfide or sulfite at 1100°F, the reference process reduction temperature. Several non-metallic materials have also been given screening tests, and graphite, alumina, magnesia, and zirconia have been found to warrant further study.

Long-term testing will continue, and the effects of water, fly ash, reducing gases, and other impurities on corrosion rates will be investigated.

C. CONTACTOR DEVELOPMENT

Wetted-wall column and baffled-tube contactor tests have been performed. The results show that mass transfer in the scrubber contactor is gas-film controlled. This knowledge makes it possible to estimate the performance of other types of scrubbers more suitable for large scale use.

The baffled-tube contactor was very efficient, and removed more than 97% of the sulfur dioxide from the test gas streams with only 36 in. of contact. However, it had a high pressure drop.

Tests with nitric oxide and sulfur dioxide in the baffled tube contactor showed that the nitric oxide was also absorbed, but that about ten times as much contactor length was required as for the sulfur dioxide. This will be studied further with more realistic gas mixtures, including oxygen, which may enhance the nitric oxide absorption rate.

Spray nozzle tests have shown that both regular open cone and aspirator type nozzles can be used; however, the test equipment was not large enough for measurements to be made of mass transfer rates to the sprayed droplets. A packed column reducer contactor is now being prepared for testing.

D. COMPONENT DEVELOPMENT

Component development work concentrated on fly ash filtration. Preliminary indications were that the fly ash was virtually insoluble in the carbonate melt, and could be removed with a sintered stainless steel filter. Further filtration and solubility tests are being performed.

Development of pumps, valves, and other components has awaited determination of suitable materials of construction.

E. PILOT PLANT AND COMPONENT TEST LOOP DESIGN

Conceptual design studies of these units has been initiated, and preliminary flow diagrams have been prepared. This work is continuing, with work on detailed flow diagrams and engineering arrangement drawings now underway.

I. INTRODUCTION

Atomics International has developed a molten carbonate process to remove sulfur oxides from power plant stack gases, which is the subject of a contract with the Public Health Service, Department of Health, Education, and Welfare. This report describes this process, and the results of the first nine months of work under Contract PH 86-67-128.

A. THE PROCESS CONCEPT

1. Flow Diagram

The flow diagram for the basic process is shown as Figure 1. In this basic process, a molten mixture of alkali metal carbonates is used to scrub the stack gases. The sulfur oxides in the stack gases react with the carbonates to form sulfites and sulfates, which remain dissolved in excess carbonate. The molten carbonate-sulfite-sulfate salt mixture is then regenerated chemically, converting the sulfite and sulfate back to carbonate and the sulfur to hydrogen sulfide. The carbonate is then recirculated to the scrubber to continue the process.

2. Process Chemistry

The carbonate mixture used to scrub the stack gases is the eutectic mixture of lithium, sodium, and potassium carbonates, i.e. 32 wt % Li_2CO_3, 33 wt % Na_2CO_3, and 35 wt % K_2CO_3. It has a melting point of 747°F (397°C), and in the molten state is a clear, mobile liquid.

In the flue gas scrubber it will be necessary to keep the temperature of the molten salt, and the incoming stack gas, above the freezing point of the carbonate mixture. In actual practice, the molten salt (melt) will be kept at 800°F or above, to provide at least a 50°F operating

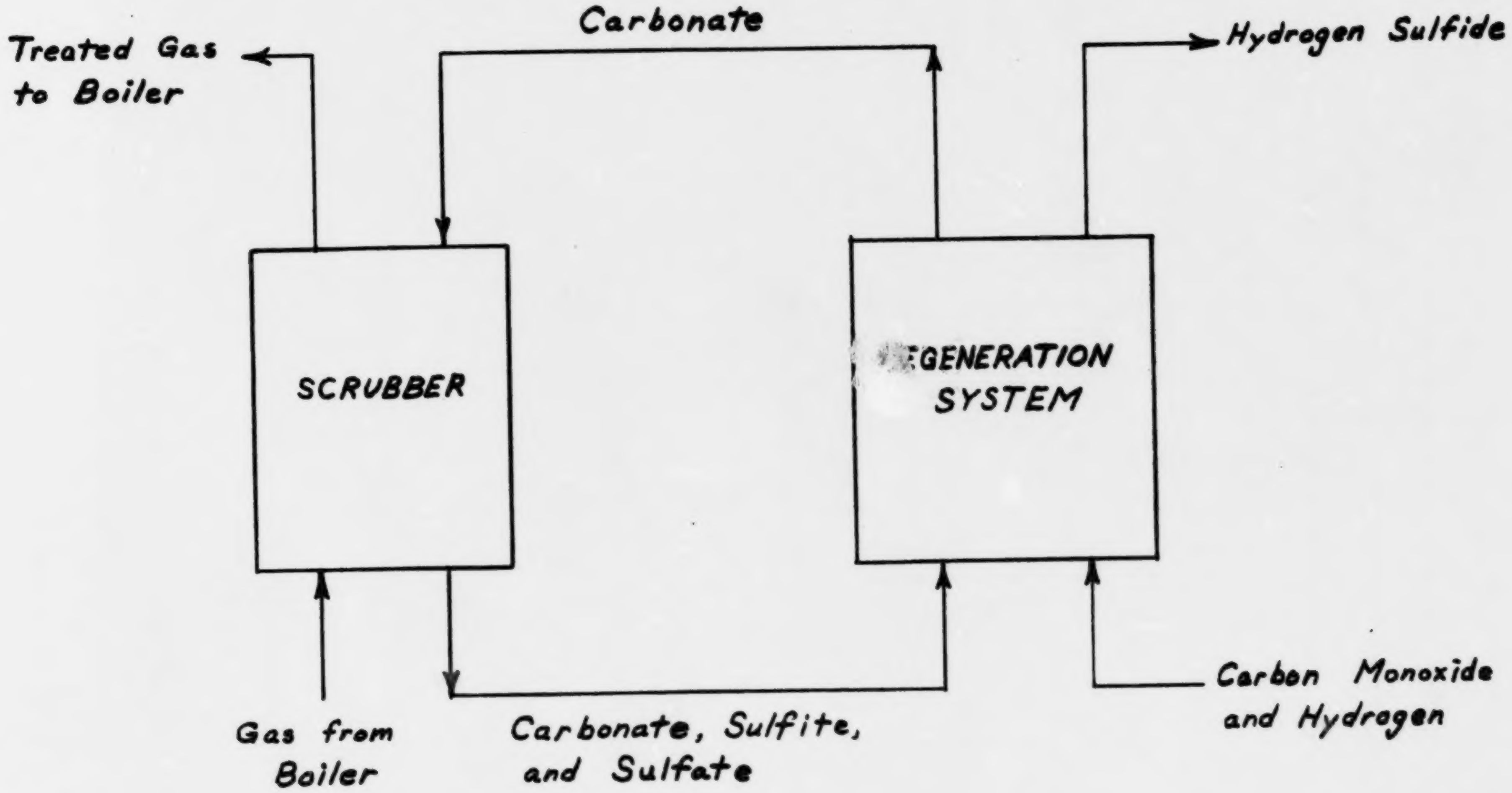

Treated Gas to Boiler
Carbonate
Hydrogen Sulfide
SCRUBBER
REGENERATION SYSTEM
Gas from Boiler
Carbonate, Sulfite, and Sulfate
Carbon Monoxide and Hydrogen

Fig. 1. Basic Process Flow Diagram

margin above the melting point. At 800°F, the eutectic carbonate melt has the physical property values listed in Table 1.

TABLE 1

PROPERTIES OF CARBONATE MELT AT 800°F (427°C)

Property	Value
Viscosity	12 cp
Specific Gravity	2.0
Specific Heat	0.40
Thermal Conductivity	~ 0.24 Btu/hr,ft,°F

The viscosity of the melt is about midway between that of water (~ 1 cp) and ethylene glycol (~ 25 cp). The other values are closer to those of water; i.e. density twice as high, specific heat 40% as high, and thermal conductivity about 70% as high as water at room temperature. It is anticipated that the physical properties of the melt will not cause any problems with pumping, spraying, heating, or using it in any other way as the process liquid.

When the stack gases are scrubbed with the molten carbonate melt, the sulfur dioxide and sulfur trioxide react with the carbonate to form sulfite and sulfate, according to the reactions

$$SO_2(g) + M_2CO_3(\ell) \rightarrow M_2SO_3(\ell) + CO_2(g) \tag{1}$$

$$SO_3(g) + M_2CO_3(\ell) \rightarrow M_2SO_4(\ell) + CO_2(g) \tag{2}$$

where M stands for the mixture of lithium, sodium, and potassium cations and (ℓ) and (g) refer to the liquid and gaseous state, respectively.

The standard free energies of reactions 1 and 2 are -9 and -54 kcal/mole, respectively, showing that the thermodynamics of the scrubbing reactions are quite favorable. In addition, both reactions are very rapid. It has been determined that over 30 wt % of the carbonate can be converted to sulfite and sulfate without causing the melting point of the resulting mixture to exceed 800°F.

While all stack gases from coal combustion contain some sulfur trioxide, sulfur dioxide is always present in far larger amounts; thus the concentration of sulfite should far exceed that of sulfate in the melt leaving the scrubber. However, it is also possible for the sulfite in the scrubber to be oxidized to sulfate by oxygen in the stack gas. This reaction,

$$M_2SO_3(\ell) + 1/2\ O_2(g) \rightarrow M_2SO_4(\ell) \qquad (3)$$

is not as rapid as reaction 1, but does occur to a significant extent. Thus, the salt melt leaving the scrubber will contain large amounts of both sulfite and sulfate, and both must be regenerated to carbonate.

In the regenerator, the sulfite and sulfate must be converted into carbonate and hydrogen sulfide. Theoretically, this can be accomplished in one step, by reacting the salts with a mixture of carbon monoxide and hydrogen, such as producer gas or reformed natural gas. The reactions are

$$M_2SO_3(\ell) + H_2(g) + 2CO(g) \rightarrow M_2CO_3(\ell) + H_2S(g) + CO_2(g) \qquad (4)$$

$$M_2SO_4(\ell) + H_2(g) + 3CO(g) \rightarrow M_2CO_3(\ell) + H_2S(g) + 2CO_2(g). \qquad (5)$$

The free energies of reactions 4 and 5 are negative, so the thermodynamics of a one-step regeneration is favorable. However, the reduction step is quite slow below a temperature of 1100°F, while the conversion to carbonate proceeds better at 800°F. Therefore in practice, it is better to carry out the regeneration in two steps; first a reduction of the sulfite and sulfate to sulfide, and then a conversion of the sulfide to carbonate plus hydrogen sulfide.

When the melt is heated to 1100°F, the sulfite disproportionates rapidly to sulfate and sulfide according to the reaction

$$4M_2SO_3(\ell) \rightarrow M_2S(\ell) + 3M_2SO_4(\ell). \qquad (6)$$

Consequently, the reduction step primarily involves the reduction of sulfate dissolved in a melt of carbonate and sulfide. This reduction can be done with different reducing agents. The reactions with hydrogen, carbon monoxide, and carbon are given below; they are similar except for the gases produced.

$$M_2SO_4(\ell) + 4H_2(g) \rightarrow M_2S(\ell) + 4H_2O(g) \qquad (7)$$

$$M_2SO_4(\ell) + 4CO(g) \rightarrow M_2S(\ell) + 4CO_2(g) \qquad (8)$$

$$M_2SO_4(\ell) + 2C(s) \rightarrow M_2S(\ell) + 2CO_2(g). \qquad (9)$$

Here (s) stands for the solid state.

After the reduction, conversion to carbonate is accomplished by treatment of the sulfide-containing melt with a mixture of steam and carbon dioxide, at about 800°F. The reaction is

$$M_2S(\ell) + H_2O(g) + CO_2(g) \rightarrow M_2CO_3(\ell) + H_2S(g). \qquad (10)$$

The carbonate, still molten, is then recirculated to the scrubber while the hydrogen sulfide is recovered for conversion into either elemental sulfur or concentrated sulfuric acid.

3. Special Features

The molten carbonate process has several inherent special features which make it attractive. These are:

(1) The absorbent medium is a liquid, so it can be handled easier than a solid material, and it does not depend on structural or surface properties for its effectiveness.

(2) The absorbent reacts irreversibly with the sulfur oxides, so theoretically all of the sulfur oxides can be removed.

(3) The absorbent reacts very rapidly with the sulfur oxides, so that contact times can be short and compact scrubbers can be used.

(4) A substantial fraction of the carbonate can be allowed to react with the sulfur oxides, so that large volumes of gas can be treated with relatively small amounts of melt.

(5) The scrubbing can be done isothermally, and at a high temperature (800°F, well above the acid dew point of the stack gas) so that (a) boiler heat is not lost, (b) the stack gases do not become highly corrosive, and (c) the stack gases retain their buoyancy and can be dispersed readily into the atmosphere after the waste heat is recovered.

(6) The molten carbonate will also remove nitrogen oxides from the stack gases, without any interference to the process.

(7) The reducing material used in regeneration is completely isolated from the hot, oxygen-containing stack gases by the liquid "seals" of melt-filled pipes, so there is no danger of fire or explosion from mixing.

These special features all combine to make the molten carbonate concept appear quite attractive for development into a commercial process to control sulfur oxide emissions. The concept was developed at

Atomics International under company sponsorship, and the development continued with HEW support under Contract PH 86-67-128. The initial development program is discussed in the following section.

B. THE DEVELOPMENT PROGRAM

The feasibility of the basic process was demonstrated in a company-sponsored program, in which the absorption reactions were found to proceed rapidly, and both one-step and two-step regenerations were accomplished. Work was begun under Contract PH 86-67-128 to study, evaluate, and further develop this basic process. The development requirements and the initial program called for under this contract are described below.

1. Development Requirements

Initial development requirements were in the areas of process chemistry, materials of construction, and contactor and component development.

In process chemistry, reaction rates needed to be determined, especially the rate of the reduction reaction, which appeared to be slow. The effect of impurities, such as fly ash, on the process chemistry also needed to be investigated.

Materials of construction had to be found which could be used to contain the different process melts, under the temperatures and conditions expected in a typical commercial installation.

The initial development program called for effort in all four of these areas, with emphasis on process chemistry. The goal was to define a "reference process", which would be feasible and attractive while still subject to further improvement. This goal has been accomplished during the initial program called for under the HEW contract. This initial program is described in the following subsection. The accomplishments made through February, 1968, are described in detail in Section II.

2. Initial Development Program, Under Contract Ph 86-67-128

Work began under this contract on June 1, 1967, in the four general areas of (1) Process Chemistry, (2) Corrosion Studies, (3) Contactor Development, and (4) Component Development. The first contract was for 9 months; it expired February 28, 1968. A revision to this contract was later negotiated, specifying more work. The revised contract also expired February 28, 1968.

Under the revised contract, the following work was specified:

a. Process Chemistry

(1) Explore the chemistry of the absorption and regeneration reactions

(2) Carry out absorption tests with SO_2-CO_2 mixtures and with synthetic flue gas

(3) Conduct regeneration tests using producer gas (CO-H_2 mixtures), hydrogen, and carbon at several temperatures, and also using catalysts

(4) Study process cycle effects by passing the same carbonate melt through the absorption-regeneration cycle several times, and

(5) Measure physical properties of the melts as needed.

b. Corrosion Studies

(1) Conduct short-term static screening tests to find promising materials

(2) Conduct long-term dynamic tests of promising materials, including tests in carbonate melts containing sulfide and sulfite, at 950°F and 1100°F, for periods of at least 1500 hours.

c. Contactor Development

(1) Test absorber contactors including wetted wall contactors

(2) Perform tests to study the effect of nitrogen oxides and fly ash on the absorption process

(3) Test regenerator contactors.

d. Component Development

Study filters, pumps, and other components as far as warranted by the results of the other tests. In addition, initiate analyses and conceptual design studies of a small pilot plant and a component test loop.

All of these requirements have been completed. The results of this initial development program are described in detail in the following section.

II. RESULTS

A. PROCESS CHEMISTRY

Initial work at Atomics International had established the feasibility of the process, including the absorption and regeneration steps, and had shown that the absorption reaction was very rapid. Under contract PH 86-67-128, the process chemistry was investigated further, with emphasis on reaction rate studies rather than on thermodynamic studies. However, it was first necessary to develop an accurate, convenient method for analyzing samples of the melts which occur in the different steps of the process.

1. Analytical Methods

The salt samples taken during process chemistry tests must be analyzed for carbonate, sulfide, sulfite, sulfate, and total sulfur content. There are satisfactory wet-chemistry methods for each of these determinations, but they are generally time-consuming and laborious. Because of this, a simple gas chromatographic technique was developed to determine carbonate, sulfite, and sulfide concentrations. The analysis was done by treating the fused salt sample with an acid, collecting the evolved gases, and analyzing the gas mixture for carbon dioxide, sulfur dioxide, and hydrogen sulfide with a gas chromatograph. While this technique is convenient and rapid, special care had to be taken to avoid losses of gases. These losses could be caused by reaction of the hydrogen sulfide with the acid, or by dissolution of hydrogen sulfide or sulfur dioxide in the acid, or in the water evolved during the reaction of salt and acid.

Extensive tests were performed to find a suitable acid which would not react with any of the gases. The acids evaluated include trichloroacetic, phosphoric, perchloric, fluoboric, and 75% sulfuric, and mixtures of these. The best was found to be 75% sulfuric acid, primarily because the other acids reacted too slowly with the fused salt samples. The oxidation of hydrogen sulfide by 75% sulfuric acid is negligible. However, both sulfur dioxide and hydrogen sulfide are absorbed in this acid to some small extent, expecially when the solution is made more dilute by the water formed when the carbonate and sulfite react with the acid. Further, the sulfur dioxide is preferentially absorbed, so that less hydrogen sulfide is absorbed when large amounts of sulfur dioxide are present. This tends to reduce the accuracy and precision of the method somewhat. Analysis of 18 known samples indicated that the standard deviations for determination of carbonate, sulfite, and sulfide were about 1%, 6%, and 8%, respectively. This is accurate enough to follow the progress of an experiment, but it is necessary to do occasional analyses by other methods when precise sulfur balances are required.

Sulfate is determined from a separate salt sample, by acidifying it with HCl, heating it to drive off all the gases evolved by the sulfite, sulfide, and carbonate, and then precipitating and weighing the sulfate quantitatively as barium sulfate. This method has an accuracy of about ± 1%.

Total sulfur is done with a third sample, using an alkaline bromine water solution plus calcium oxide to oxidize all the sulfur-containing anions to sulfate, and then collecting and weighing the sulfate as barium sulfate. This method is quite accurate, within ± 2% for 10 known samples.

Detailed descriptions of the analytical procedures are given in Appendix A.

2. Absorption Studies

The first absorption tests (under AI funding) had all been conducted with different concentrations of sulfur dioxide in carbon dioxide carrier gas. These had shown that the absorption reaction was very rapid, and that essentially all of the sulfur dioxide could be removed. Under this contract, other absorption experiments were performed to determine the effect of oxygen, water vapor, and fly ash on the reaction and its products. A test was also done to study the absorption of sulfur dioxide from actual combustion gases.

The absorption tests were done using the apparatus shown schematically in Figure 2. The absorption reactor was a cylindrical capsule made of 2½ in. diameter type 347 stainless steel pipe, closed at each end with a butt-welded pipe cap. It was contained within an electric furnace, which kept it at the operating temperature. The molten salt formed a pool in the bottom of the reactor, and the gas stream being tested was bubbled through the melt. The remainder of the apparatus consisted of the gas supplies with flow meters and flow control valves, a humidifier for adding water vapor to the nitrogen stream when desired, and connections for sending inlet or effluent gas samples to a gas chromatograph for analysis. Melt samples were obtained during each test, by drawing them up into a quartz tube inserted through the thermocouple tee in the effluent gas line.

Four test runs were performed with this apparatus; two to study the effect of oxygen on the absorption step, one to study the effect of oxygen plus water vapor, and the fourth to study the combined effect of oxygen, water vapor, and fly ash. In each test, the melt was kept at 850°F. The remaining test conditions are listed in Table 2.

TABLE 2

ABSORPTION TEST CONDITIONS

Test	Melt Composition	Gas Composition (vol %)				Gas Flow Rate (ml/min)
		N_2	CO_2	O_2	SO_2	
1	Carbonate Eutectic	80	19	1	0.1	1080
2	Carbonate Eutectic	80	19	1	0.1	1080
3	Carbonate Eutectic	80*	19	1	0.1	1080
4	Carbonate Eutectic plus 10 wt % fly ash	76	10	5	0.3	1150

*Saturated with water at 80°C

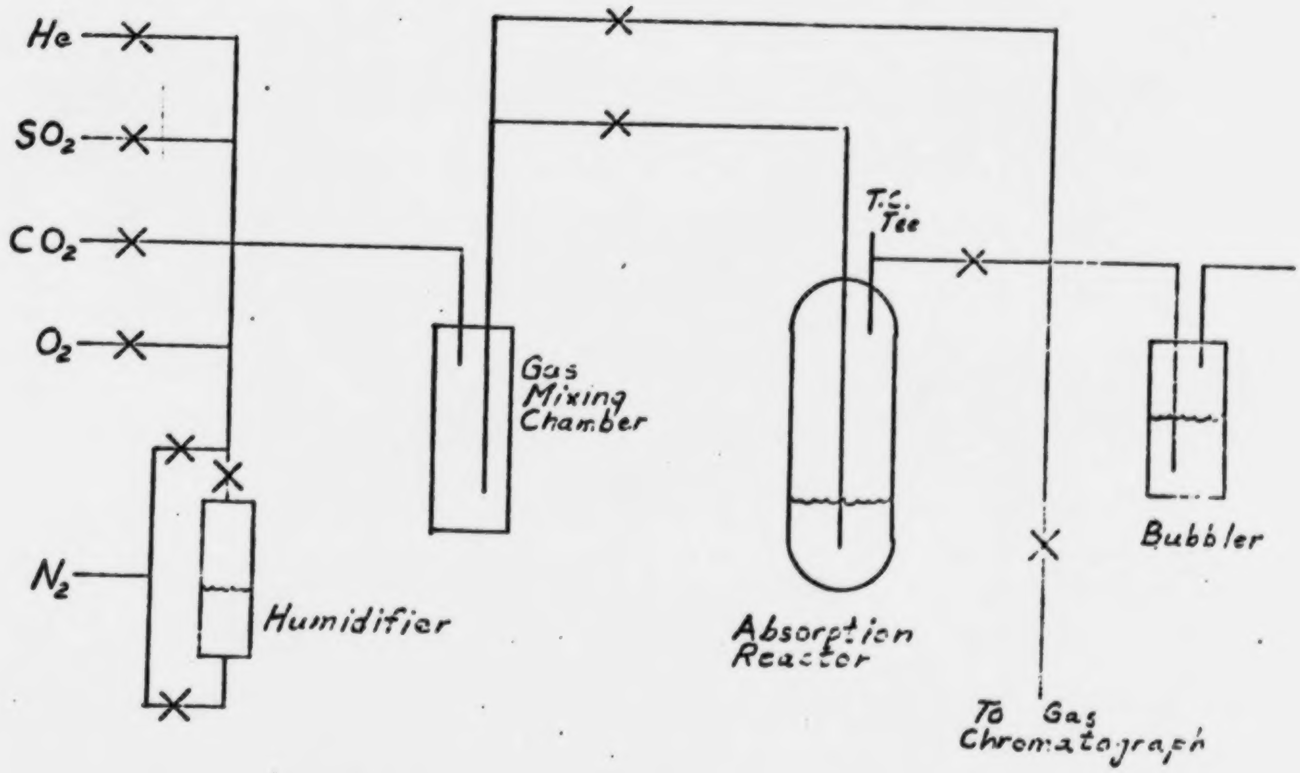

He
SO₂
CO₂
O₂
N₂
Humidifier
Gas Mixing Chamber
T.C. Tee
Absorption Reactor
To Gas Chromatograph
Bubbler

Figure 2. Absorption Test Apparatus

The exit gases and the melts were sampled periodically and analyzed during each test. The results of the melt sample analyses are listed in Table 3.

TABLE 3

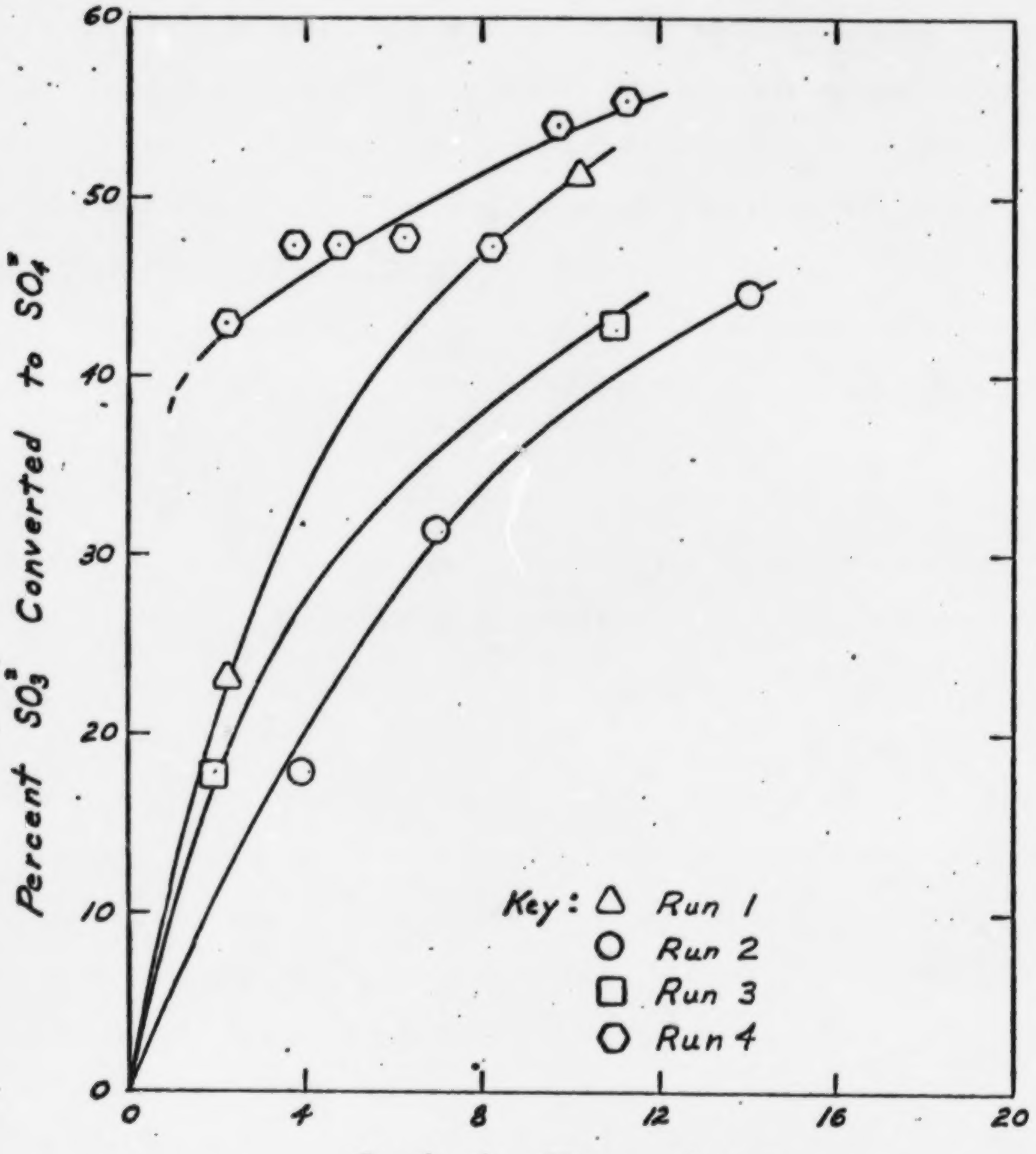
ABSORPTION TEST MELT SAMPLE COMPOSITIONS

Test	Time (hr)	Sample Composition (wt %)					% Sulfite Converted to Sulfate
		M_2CO_3	M_2SO_3	M_2SO_4	M_2S	Ash	
1	0	100	0	0	-	-	0
	2-1/4	98.2	1.05	0.36	-	-	23
	10-1/4	90.8	3.12	3.68	-	-	51
2	0	100	0	0	-	-	0
	4	95.7	0.82	0.20	0	-	18
	7	93.6	4.20	2.23	0.07	-	31
	13	84.9	8.45	3.71	0.12	-	28
	14	84.9	6.20	5.96	0.22	-	44
3	0	100	0	0	-	-	0
	2	95.1	1.52	0.37	-	-	18
	11	86.0	5.60	5.87	0.44	-	43
4	0	90	0	0	-	10.0	0
	2-1/4	89.5	1.11	0.93	0	9.1	43
	3-1/4	83.5	2.14	2.20	0.06	10.0	47
	4-1/4	83.2	3.13	3.23	0.07	14.3	47
	6-1/4	79.9	4.12	4.54	0.18	11.3	48
	8-1/4	73.2	6.30	6.89	0.32	10.9	47
	9-3/4	73.0	6.54	9.16	0.28	10.4	54
	11-1/4	69.6	7.10	10.85	0.24	10.1	56

One reason for performing the tests was to determine the rate at which the sulfite would be oxidized to sulfate, by oxygen according to reaction 3. This did occur, as evidenced by the sulfate concentrations, which increased with time. Some sulfate was also formed by disproportionation (reaction 6), since sulfide was also found in the melt samples. However, the sulfide concentrations were always small, indicating that most of the sulfate was formed by oxidation. The percent of sulfite which was converted to sulfate was calculated for each sample, and listed in Table 3. These data are also shown plotted as a function of contact (test) time in Figure 3.

Inspection of the figure shows that (1) the initial conversion rate was much higher when the gas stream contained 5% oxygen and the melt contained 10% fly ash than when only 1% oxygen was used and no fly ash was present, and (2) the presence of water vapor had no measurable effect on the conversion of sulfite to sulfate.

The 5% oxygen content of the gas stream used in the fourth test approximates that in actual flue gases, so the conversion rate under these conditions is quite important. No melt samples were taken during the first 2-1/4 hours of this test, and it is difficult to extrapolate the data to determine the rate of oxidation to be expected in a short contact time, such as will be encountered in a flowing salt contactor. It appears that conversion of over 40% of the sulfite may occur. However, the relative rates of sulfur dioxide absorption and sulfite oxidation will depend on gas-liquid mass transfer rates, which must be measured in an actual contactor, with gas and melt flowing countercurrently. Therefore, application of the sulfite conversion rates measured in bubbler-type scrubbers to



Runs 1 and 2: 80% N_2, 19% CO_2, 1% O_2, 0.1% SO_2

Run 3: Same as 1 and 2 but saturated with H_2O at 80°C

Run 4: 76% N_2, 19% CO_2, 5% O_2, and 0.3% SO_2; 10% fly ash in melt

Figure 3. Conversion of Sulfite to Sulfate

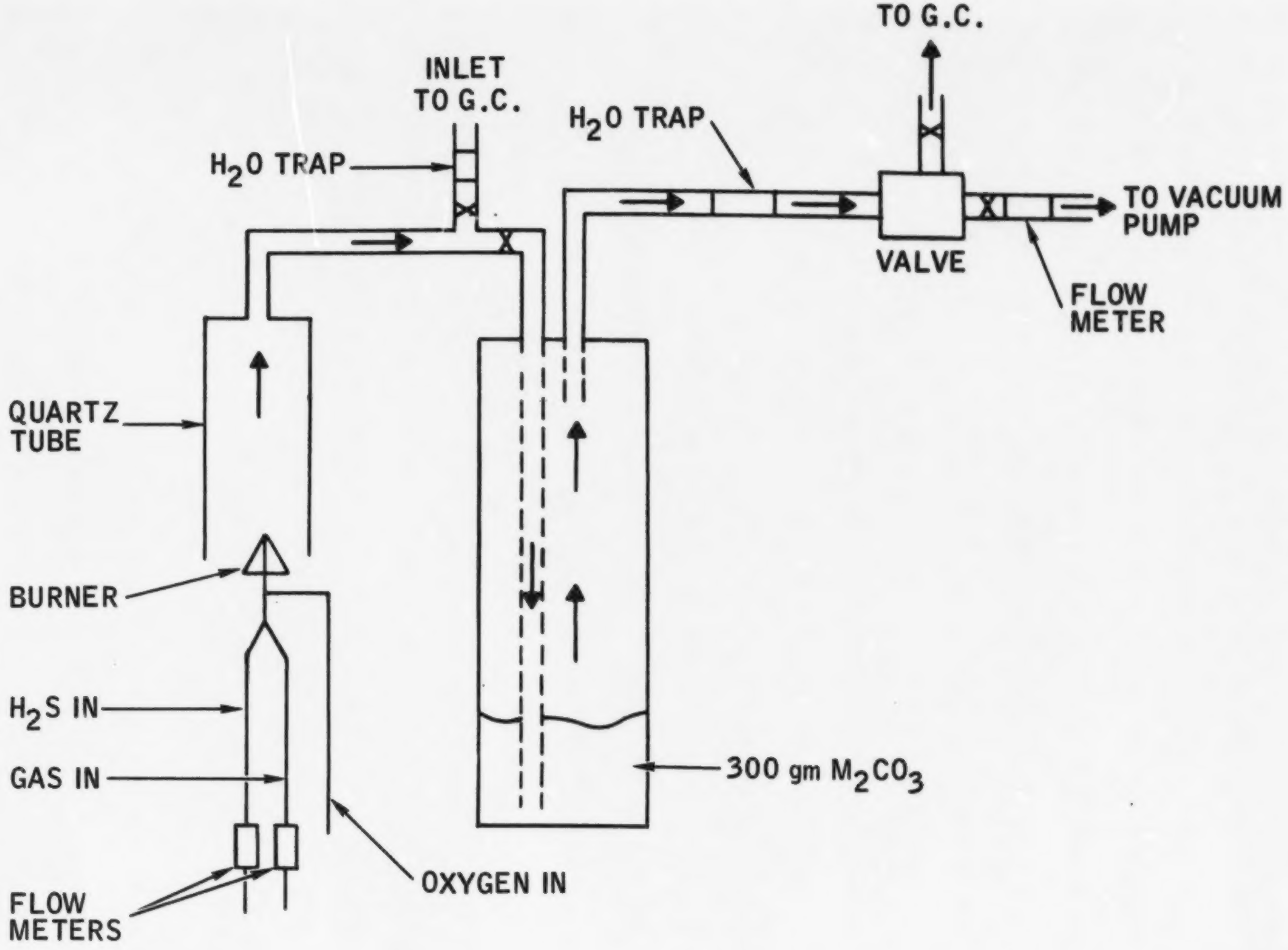
countercurrent contactors must be done with reservations, pending the results of contactor tests.

No sulfur dioxide or hydrogen sulfide was ever detected in the effluent gases from any of the four tests. These facts are quite important. The absence of sulfur dioxide shows that, based on the accuracy of the gas chromatographic analytical technique, more than 99% of the sulfur dioxide was always absorbed by the melt, and further, that this removal efficiency was not affected by the presence of fly ash, water vapor, or oxygen. The absence of hydrogen sulfide indicates that even with up to 0.4 wt % sulfide in the melt and water vapor in the gas, no hydrogen sulfide will be emitted from the scrubber contactor.

The fly ash used was obtained from the NCAPC fly ash filtration test facility in Cincinnati. Its composition is given in Appendix B.

A fifth absorption test was also performed, to study the removal of sulfur dioxide from actual combustion gases. In this test, a mixture of hydrogen sulfide and natural gas was burned with oxygen in a standard glass-blowing torch. The combustion gases were then collected in a quartz tube and passed through a bubbler containing carbonate melt. The test apparatus used is shown schematically in Figure 4.

The bubbler was maintained at 1040°F, and the gas stream was bubbled through the melt at the rate of 1 ℓ/min for 109 minutes. At first the oxygen flow rate was too low for complete combustion of the hydrogen sulfide, so that the inlet gas stream contained about 1% hydrogen sulfide. This was bubbled through the melt for about 10 minutes, and then the oxygen flow rate was increased until a large amount of excess oxygen was present. The composition of the inlet gas stream then remained relatively constant


TO G.C.
INLET
TO G.C.
H_2O TRAP
H_2O TRAP
TO VACUUM
PUMP
VALVE
FLOW
METER
QUARTZ
TUBE
BURNER
H_2S IN
GAS IN
300 gm M_2CO_3
OXYGEN IN
FLOW
METERS

7-17-68 UNCL

7732-4008

Figure 4. Absorption Test Flow Diagram

for the remainder of the test, at 49% water vapor, 24% carbon dioxide, 25% oxygen, and 2% sulfur dioxide.

During the time the hydrogen sulfide was present as 1% of the inlet gases, about 0.1% was also detected in the exit gases. This indicated that the melt was absorbing about 90% of the hydrogen sulfide. After the oxygen flow rate was increased, the hydrogen sulfide disappeared from the exit gases. No sulfur trioxide was found in either the inlet or exit gases, and no sulfur dioxide was detected in the exit gases. This demonstrated that the carbonate melt removed the sulfur dioxide from gases resulting from natural gas combustion as effectively as it did from carbon dioxide-sulfur dioxide gas streams.

After the test, the melt was analyzed and found to consist of 94.6% carbonate, 4.7% sulfate, and 0.29% sulfite. No sulfide was detected, presumably because the large amount of oxygen in the gas stream oxidized it all to sulfite and/or sulfate. Most of the sulfite was also oxidized to sulfate.

No further bubbler absorption tests with combustion gases are planned, since synthetic gas mixtures behave the same way and their composition can be controlled more easily.

3. Reduction Studies

These studies were directed toward finding the fastest practical way to reduce sulfite and sulfate (in carbonate melts) to sulfide. Reduction rates were determined in tests using carbon, hydrogen, carbon monoxide, and mixtures of hydrogen and carbon monoxide as reducing agent; with different types of equipment; and at different temperatures. The effects of different catalysts were also studied. These tests are all described below.

a. Carbon Reduction Tests

The first reduction tests were done using carbon as the reducing agent, because it is relatively inexpensive. However, the results were discouraging, because the reduction reaction rate was quite low. The best that could be accomplished with carbon was to reduce 50% of a mixture initially containing 25 wt % sulfate in 80 minutes, at 1350°F. A test at 1200°F showed 52% of the reduction completed after 4 hours, and tests at 1140°F and 930°F showed that very little reduction took place at these temperatures.

These reduction rates were too slow to be practical except at 1350°F, which is an undesirably high temperature from a materials standpoint. It may be possible to increase the carbon reduction rates by catalysis or some other means, and this should be tried in the future. However, in this initial stage of the process development program, it was necessary to first investigate other reducing agents, in order to demonstrate a rapid reduction as part of a "Reference Process." Therefore, hydrogen and carbon monoxide reductions were studied.

b. Rotating Packed Bed Contactor Tests

(1) Hydrogen Reduction Tests. The first hydrogen reduction test was a simple one, in which hydrogen gas was bubbled through a carbonate-25 wt % sulfate melt contained in a type 347 stainless steel bomb. The melt was kept at 1200°F, and the hydrogen flow rate was 300 ml/min, at 60 psig. A melt sample taken after 1 hour showed that only 33% of the original sulfate had been converted to sulfide. This was disappointingly slow.

It was thought that the reduction reaction might be diffusion controlled, and that the reaction rate could be increased if better mass transfer could be provided. To test this hypothesis, a packed bed contactor was constructed, in which a very large gas-salt interfacial area could be maintained. This contactor is shown in Figure 5. It consisted of an 8 in. piece of 2-in. diameter type 347 stainless steel pipe, closed at both ends with pipe caps, and packed with either chromium steel balls and/or small carbon steel machine screws. The gas inlet and outlet lines were 1/4 in. OD tubing, and the sample tube guide was 3/8 in. OD tubing. The interior end of this guide was made of steel screen, welded in place. This screen allowed salt to flow into the guide but kept the packing out. The salt trap was provided to catch any salt forced out of the contactor by the gas, so that salt would not solidify in the outlet tube and plug it.

In operation, the contactor and salt trap were mounted inside an electric furnace, and rotated about the inlet tube - outlet tube axis at about 11 rpm. The melt containing the sulfite and/or sulfate was contained within the packing, filling about half of the packing voids. As the contactor rotated, four vanes inside the tube continually carried salt up to the top of the packed bed and allowed it to flow back down through the packing. Thus, the melt presented a large, mobile, and constantly renewed surface to contact with the hydrogen gas being passed through the packing. It should also be noted that a large amount of iron surface was present. As subsequent results showed (see section (3) below) the iron evidently catalyzed the reduction reaction.

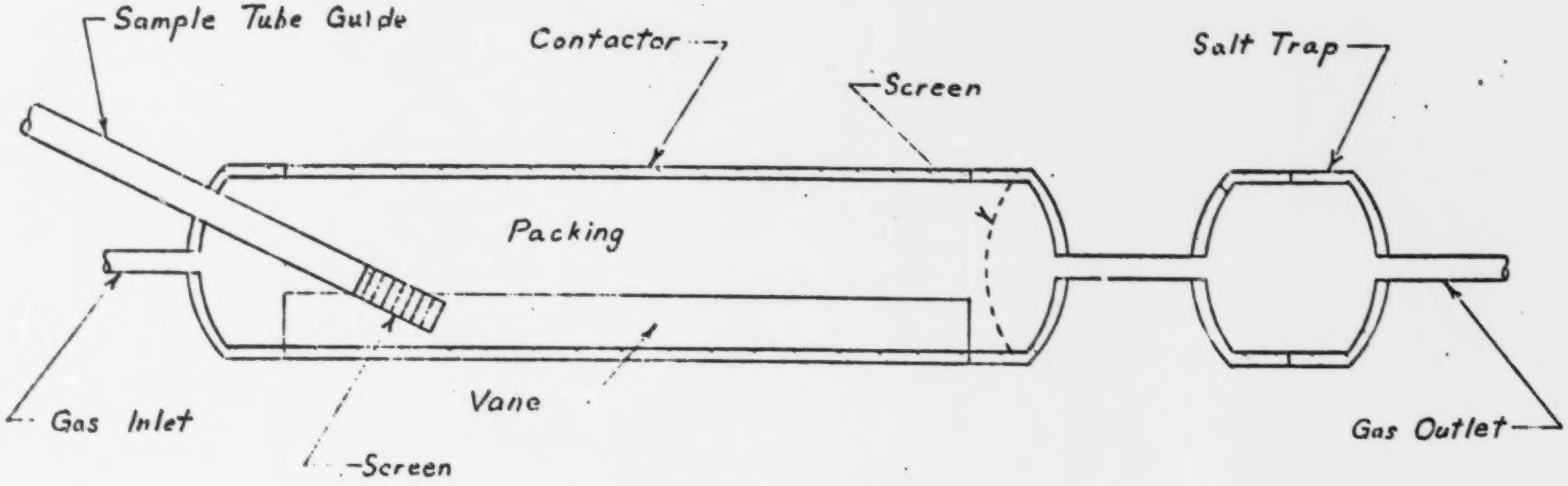

Sample Tube Guide
Contactor
Salt Trap
Screen
Packing
Gas Inlet
Vane
Screen
Gas Outlet

Figure 5. Rotating Packed Bed Contactor

Five hydrogen reduction tests were performed with this type of contactor and the steel packing. Three were done at 1110°F (600°C), and one each at 980°F (525°C) and 1290°F (700°C) to study the effect of temperature on reaction rate. A sixth test was done with the rotating packed bed contactor packed with graphite raschig rings, to investigate the effect of iron on the reaction.

In the first test done with steel packing at 1110°F, the melt was initially 26.2 wt % sulfate in carbonate, while in the other two tests the contactor was initially loaded with carbonate eutectic only and then sulfite was formed in situ by passing pure SO_2 gas into it. The experimental conditions for the three 1110°F tests are summarized in Table 4.

TABLE 4

EXPERIMENTAL CONDITIONS

HYDROGEN REDUCTIONS AT 1110°F (600°C), 1 atm

	First Test	Second Test	Third Test
Starting Material	26.2% M_2SO_4 in 240 g melt	0.6 moles SO_2 reacted with 270 g eutectic	0.6 moles SO_2 reacted with 240 g eutectic
Hydrogen Flow Rate	1.5 ℓ/min	3 ℓ/min	3 ℓ/min
Packing	Chrome-steel balls and screws	Re-used packing from first test	Screws only

During the tests, samples of salt were periodically withdrawn through the sample tube guide and analyzed. The water evolved during the first test was also collected in a bed of magnesium perchlorate and weighed, whenever a salt sample was taken. The results obtained for the first test are listed in Table 5.

TABLE 5

FIRST TEST - HYDROGEN REDUCTION OF SULFATE AT 1110°F (600°C)

Time (min)	Sample Composition (wt %)				H_2O (grams)	Percent Reduced Based on M_2S Produced[2]	Percent Reduced Based on M_2SO_4 Remaining[2]
	M_2CO_3	M_2S	M_2SO_3	M_2SO_4			
0	75.7	0.65	0	25.2	0	4.4	0
10	72.7	3.1	0	20.6	3.6	20.8	18.3
20	79.5	8.5	0	8.9	7.8	57.0	64.7
35	79.4	12.7	0	1.2	10.6	85.3	95.4
65	80.7	14.0	0	0	11.9	94.0	100.0
100% Redn	85.1	14.9	0	0	31.7	100	100

The fractional amount of sulfate reduced was calculated from both the amount of sulfide formed and from the amount of sulfate removed. These values are listed in the last two columns of the table, and also shown plotted as a function of time in Figure 6.

The curves of Figure 6 show that reduction was rapid, and that the sulfate was completely removed in less than 50 min. Only 94% of the theoretical sulfide concentration was found after 65 min; however, this may well have been 100%, within the experimental accuracy of the sulfide analysis technique.

It should be noted that whereas 31.7 grams of water should have been evolved when the reduction was complete, only 11.9 grams (38%) was actually collected in the magnesium perchlorate after 65 min. This

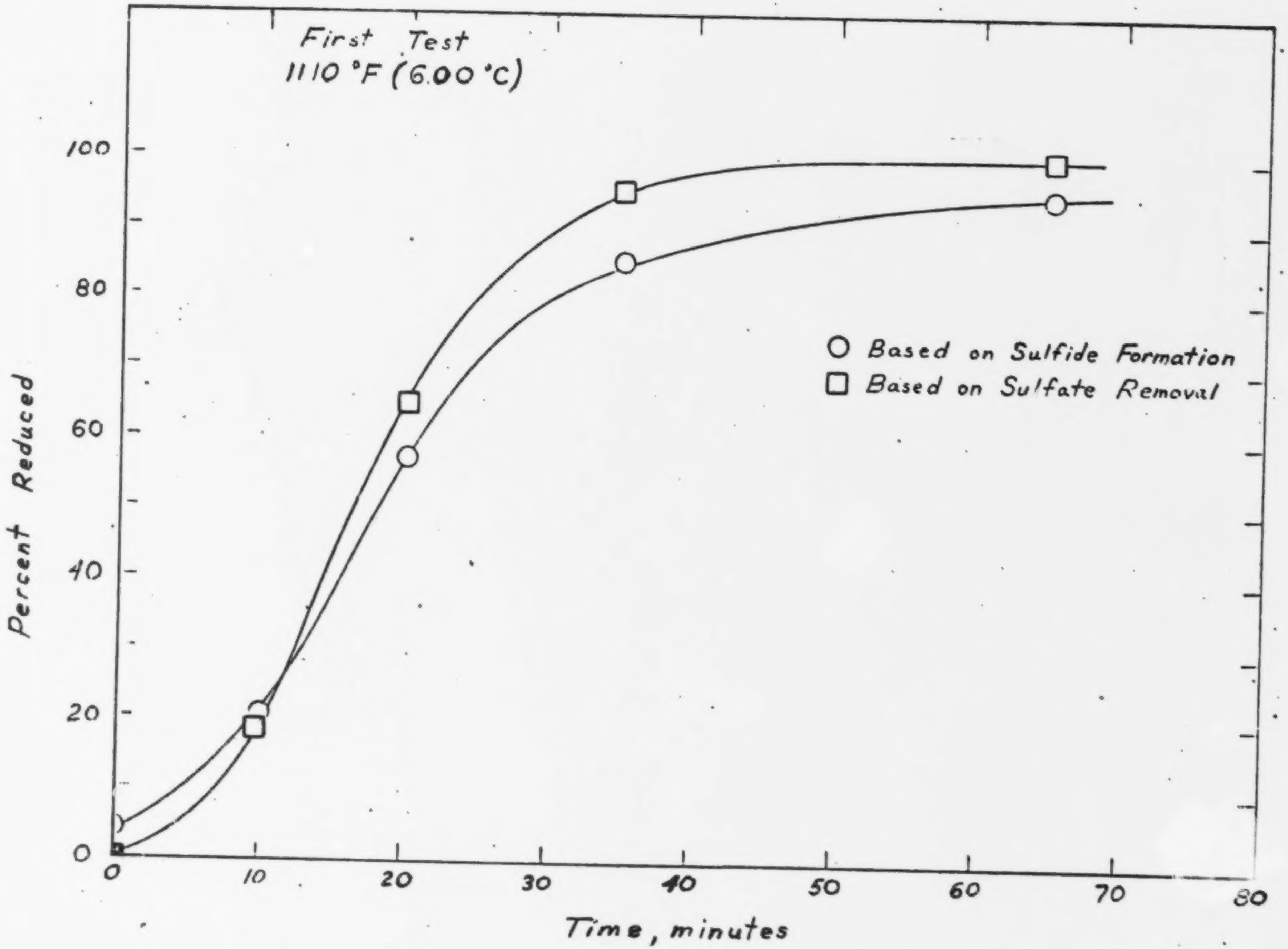


Figure 6. Reduction of Sulfate with Hydrogen

may have been caused by retention of water in the melt, or by reduction by iron or other materials. It is discussed further below.

In the second test at 1110°F, salt solidified in the exit gas line after 40 min and caused the test to be terminated. The data obtained during the first 40 min are listed in Table 6.

TABLE 6

SECOND TEST - HYDROGEN REDUCTION OF SULFITE AT 1110°F (600°C)

Time (min)	Sample Composition (wt %)				Percent Reduced Based on Sulfide Produced
	M_2CO_3	M_2S	M_2SO_3	M_2SO_4	
0	99.7	0	0	0	0
0*	80.3	0.24	14.6	7.3	0
20	82.6	4.2	0	-	32.6
40	75.5	7.2	0	-	56.0

*After absorption of SO_2. Total sulfur is 12.87 wt % as M_2S.

The results of the third test are listed in Table 7.

TABLE 7

THIRD TEST - HYDROGEN REDUCTION OF SULFITE AT 1110°F (600°C)

Time (min)	Sample Composition (wt %)				Percent Reduced Based on M_2S Produced	Percent Reduced Based on M_2SO_4 Remaining
	M_2CO_3	M_2S	M_2SO_3	M_2SO_4		
0	98.3	0	0	0	0	0
0*	79.3	Trace	7.5	13.3	0	0
10	81.8	1.5	0	15.7	11.2	32.3
25	84.9	5.0	0	9.1	37.3	60.8
45	87.6	8.9	0	1.3	66.4	94.5
75	84.8	12.5	0	0	93.3	100.0

*After absorption of SO_2 (total S is 23.2% as wt % M_2SO_4)

Examination of the sample compositions of the second and third tests shows that the sulfite initially present was rapidly disproportionated to sulfide and sulfate. As in the first test, the fractional amount of reduction was calculated, based on both the rate of formation of sulfide and the rate of removal of sulfate for the third test, and on the rate of sulfide formation alone for the second test. These data are listed in Tables 6 and 7 and shown plotted as a function of time in Figure 7. The reduction rates for these two tests were slightly slower than those achieved in the first test, but still quite rapid. The sample analyses indicate that the sulfate was removed somewhat faster than the sulfide was formed, possibly indicating the formation of reaction intermediates.

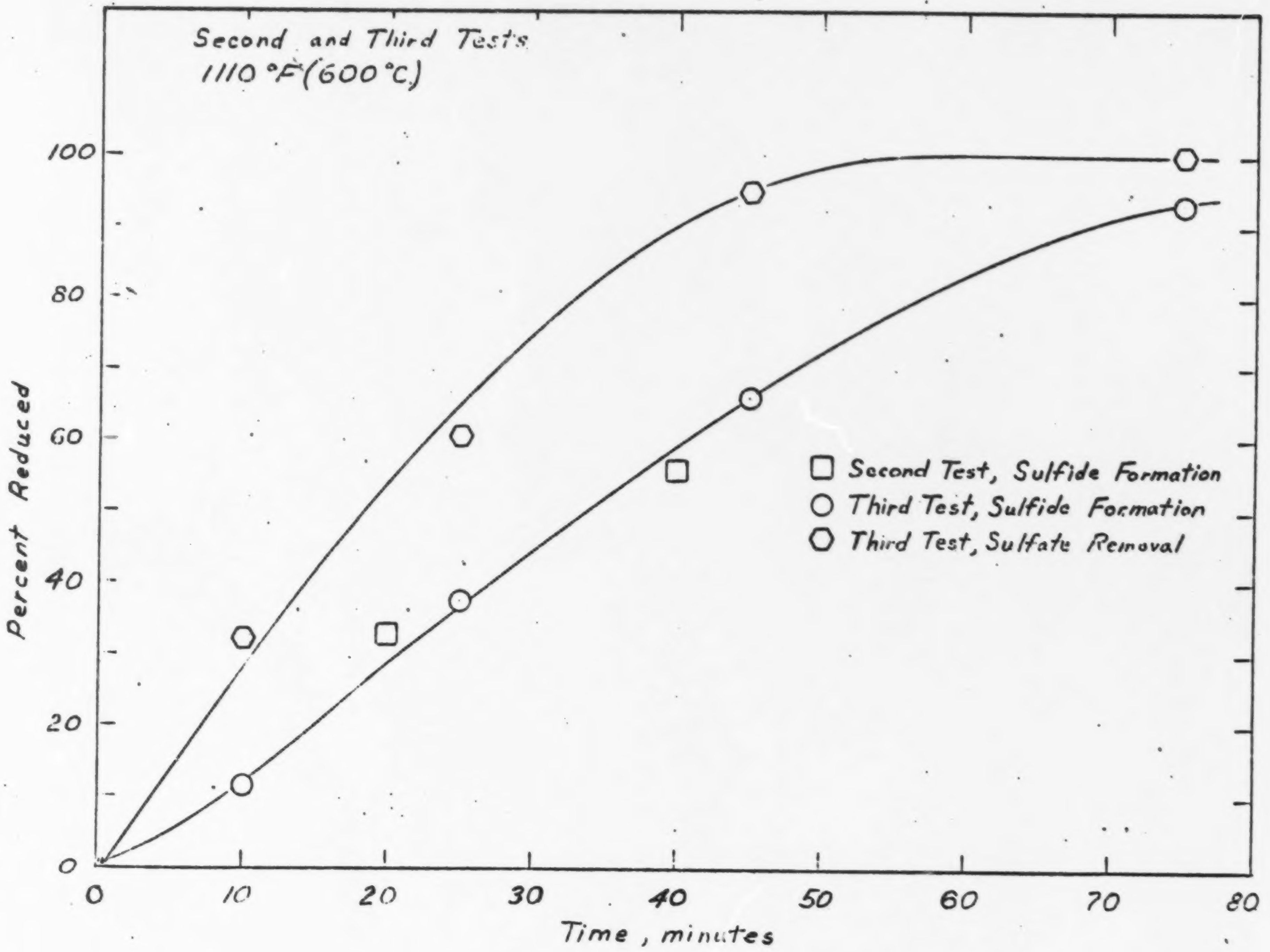


Figure 7. Reduction of Sulfate-Sulfite with Hydrogen

These three tests resulted in much faster reductions than were obtained in the first (bubbler) test at 1200°F, indicating that the enhanced gas-liquid mass transfer and/or the large iron surface area increased the reduction reaction rate.

The tests done at 980°F and 1290°F were done under the same conditions as the 1110°F tests, so that the only variable changed was the temperature. The results of analyses of the salt sample from the 980°F test are given in Table 8.

TABLE 8

HYDROGEN REDUCTION OF SULFATE AT 980°F (525°C)

Time (min)	Sample Composition (wt %)				Percent Reduced Based on M_2S Produced	Percent Reduce Based on M_2SO_4 Remaining
	M_2CO_3	M_2S	M_2SO_3	M_2SO_4		
0	74.6	1.0	0	22.4	0	0
30	70.5	1.8	0	18.2	6.8	18.7
60	66.9	2.5	0	15.3	12.7	31.7
90	67.2	2.7	0	13.0	14.4	42.0
120	79.3	3.4	0	11.4	20.3	49.0
165	73.5	4.2	0	8.8	27.1	60.8
210	74.8	4.7	0	6.7	31.3	70.2
255	75.2	5.9	0	4.5	41.5	80.0
315	80.5	6.7	0	2.6	48.3	88.4
100% Redn	88.2	11.8	0	0	100	100

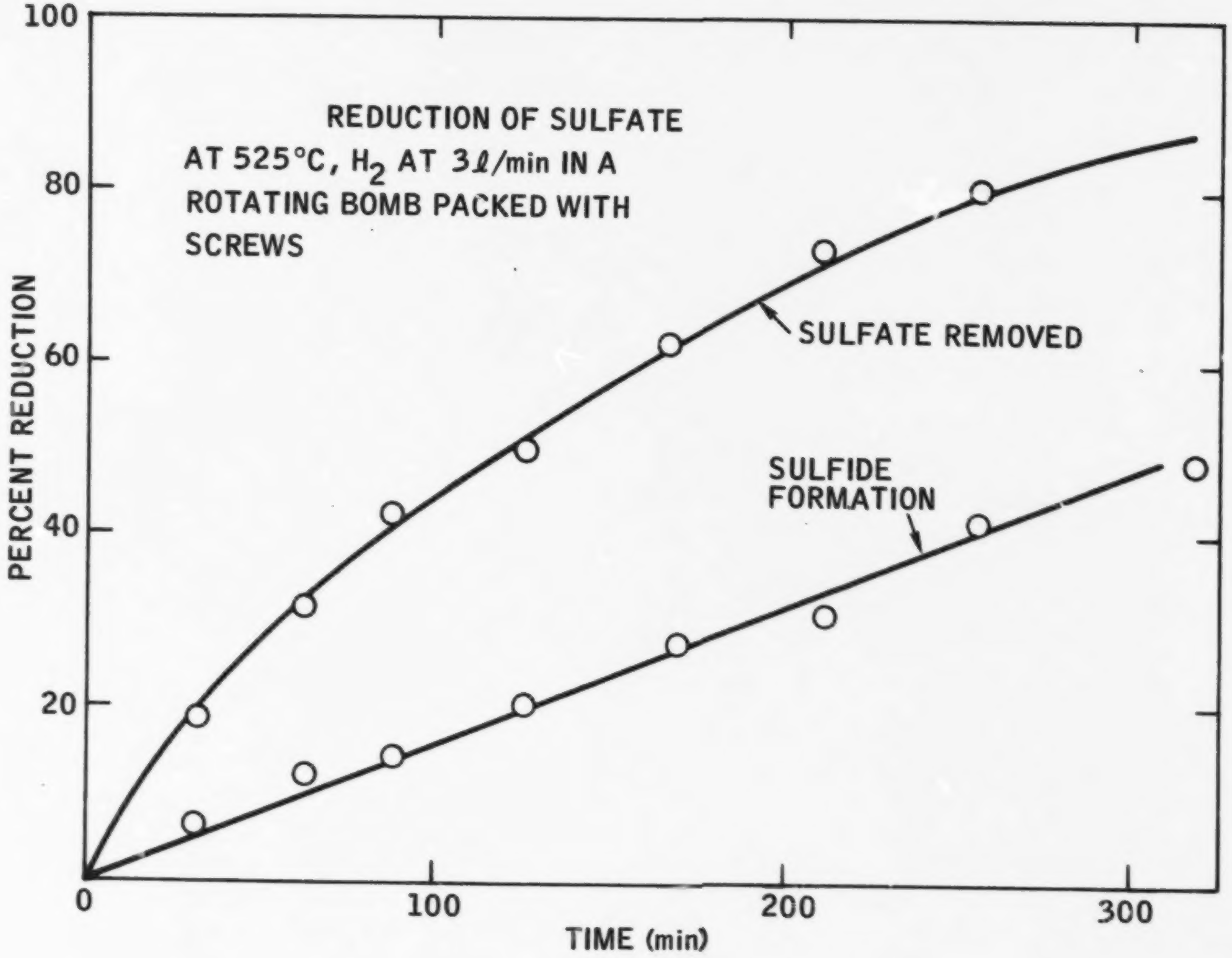
The percent completion based on sulfide formation and sulfate removal was also calculated for each salt sample, and listed in Table 8. These data are also shown plotted in Figure 8; they show that the rate of reduction was considerably slower than at 1110°F. The sulfide content was much lower than expected, possibly indicating that other sulfur-containing intermediates were produced that were not completely reduced to sulfide at this temperature. Over 50% of the sulfur was not present as sulfide at the end. This is a much larger amount than was missing in the tests done at 1110°F.

The results of the analyses of the samples from the test at 1290°F are listed in Table 9, together with the percent completion for each sample calculated from the amount of sulfate remaining.

TABLE 9

HYDROGEN REDUCTION OF SULFATE AT 1290°F (700°C)

Time (min)	Sample Composition (wt %)				Percent Reduced Based on M_2SO_4 Remaining
	M_2CO_3	M_2S	M_2SO_3	M_2SO_4	
0	74.0	7.5	0	11.8	0
6	78.9	13.0	0	4.9	58.5
12	71.3	16.6	0	Trace	100
18	66.2	18.6	0	0	100
100% Red'n	85.5	14.5	0	0	100



7-17-68 UNCL

7732-4009

Figure 8. Sulfate Reduction with Hydrogen at 980°F (525°C)

The initial melt for this test was formulated to contain approximately 23 wt % sulfate, but only 11.8 wt % was found in the first sample. The iron in the packing and container may have reduced the missing sulfate during the heat-up time and also during the time (~ 1.5 hours) when the melt was maintained at about 1290°F before the hydrogen flow was started. Iron may have been responsible for part of the reduction in the tests at 1110°F, also. This is also suggested by the fact that only 38% of the theoretical amount of water was evolved and collected during the first 1110°F test. It is possible that part of the reduction was caused by the iron in the packing, according to the reaction

$$M_2SO_4 + 4Fe \rightarrow M_2S + 4FeO. \qquad (11)$$

No water is evolved as a byproduct of this reaction. The effect of iron on the reduction reaction was studied in detail, and is reported in Section 3-c below.

The percent completion of the reduction at 1290°F was calculated based on the amount of sulfate present in the first sample (11.8 wt %); the percent completion based on sulfide formation was not calculated due to the large amount of sulfide formed before the hydrogen reduction started.

The percent completion values for this test are shown plotted versus time after hydrogen contact started in Figure 9. The reduction was essentially complete after 12 minutes.

A comparison of the reaction rates at 980°F (525°C), 1110°F (600°C) and 1290°F (700°C) shows that the rate increased by a factor of ~ 5 for each 100°C increase in temperature. The half-life values for the reactions are listed in Table 10.

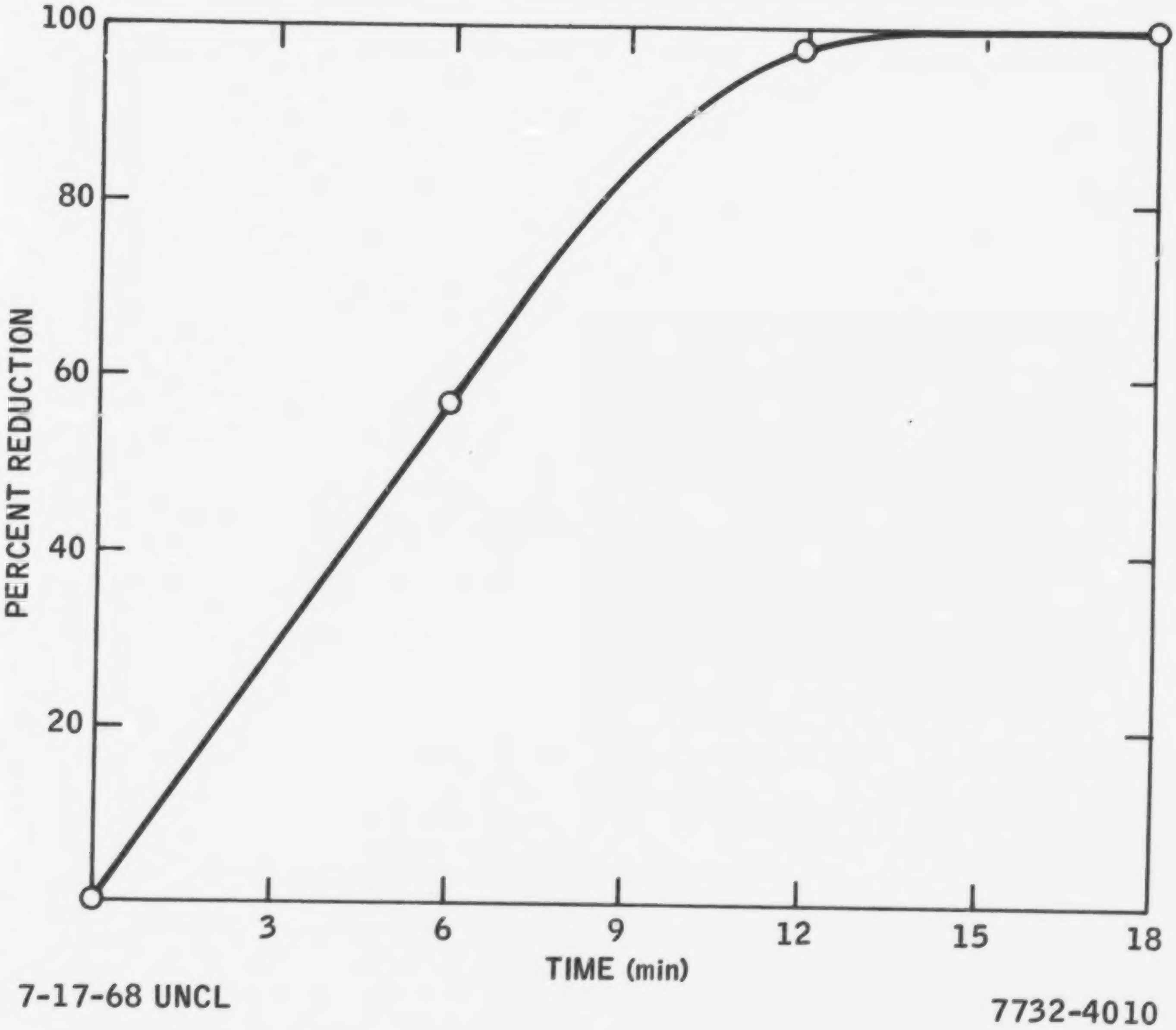


Figure 9. Sulfate Reduction with Hydrogen at 1290°F (700°C)

TABLE 10

HALF-LIFE VALUES OF HYDROGEN REDUCTION REACTIONS

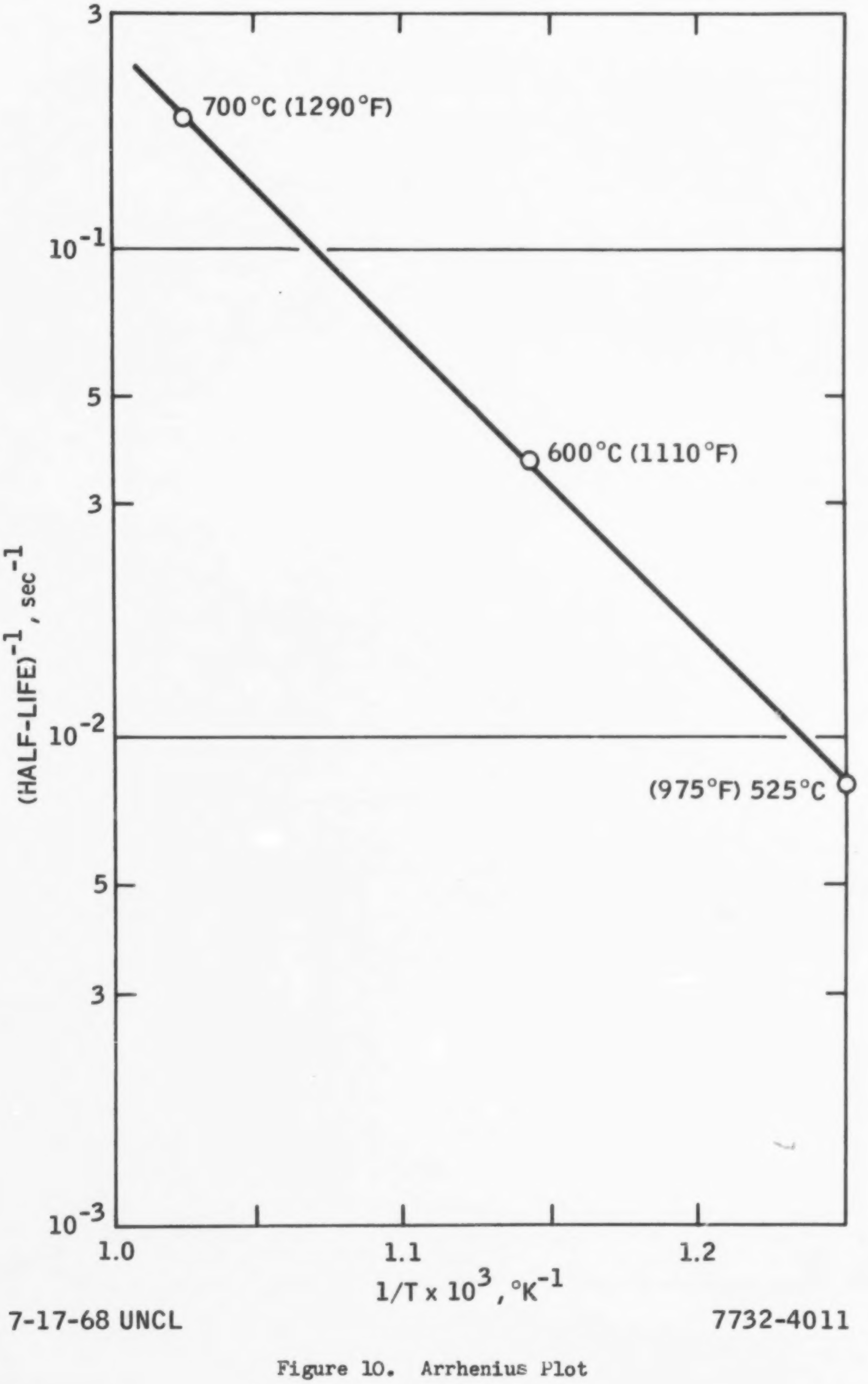
Temperature (°C)	Half-Life (min)	$(\text{Half-Life})^{-1}$ $(\text{min})^{-1}$
525	124	0.0080
600	27	0.037
700	5.4	0.185

The last column lists the reciprocal of the half-life, which is approximately equal to the first-order reaction rate constant, k. The rate constant, in turn, is given by the Arrhenius equation:

$$k = A \exp(-E_a/RT) \tag{12}$$

A plot of the logarithm of the reciprocal of the reaction half-life ($\simeq k$) versus T^{-1} is given in Figure 10. The relationship is linear, indicating that the reaction is first-order with respect to sulfate. From the slope of the plot, the activation energy, E_a, was found to be 28 kcal/mole. This is a rather low value, probably due to catalysis by the iron.

The results of the previous tests gave many indications that the iron in the contactor packing was taking part in the reduction reaction. To study this further, a hydrogen reduction test was done using 1/4-in. graphite raschig rings as packing, in a type 347 stainless steel rotating packed bed contactor. The experimental apparatus and procedure were identical with those used in the previous reduction tests. The test conditions were as listed in Table 11.



7-17-68 UNCL

7732-4011

Figure 10. Arrhenius Plot

TABLE 11

TEST CONDITIONS, HYDROGEN REDUCTION WITH GRAPHITE PACKING

Starting Material	25.4 wt % M_2SO_4 in M_2CO_3
Temperature	1110°F (600°C)
Pressure	1 atm
H_2 Flow Rate	2.7 ℓ/min

As before, salt samples were taken periodically and analyzed. The compositions of these samples are listed in Table 12. Also, the fractional amount of sulfate reduced was calculated for each sample, based on both the amount of sulfate removed and the amount of sulfide formed. These data are also listed in Table 12, and shown plotted as a function of time in Figure 11.

TABLE 12

TEST RESULTS, HYDROGEN REDUCTION WITH GRAPHITE PACKING AT 1110°F

Time	Sample Composition (wt %)			Percent Completion Based on:	
	M_2CO_3	M_2SO_4	M_2S	M_2SO_4 Removal	M_2S Formation
0	79.5	25.4	0	0	0
25	77.4	24.9	0.25	2.0	1.7
70	79.2	23.3	1.59	8.3	11.0
100	80.8	20.5	3.08	19.3	21.4
145	80.3	12.6	7.4	50.4	52.0
190	86.6	0.8	13.8	97.0	95.8
100%	85.6	0	14.4	100	100

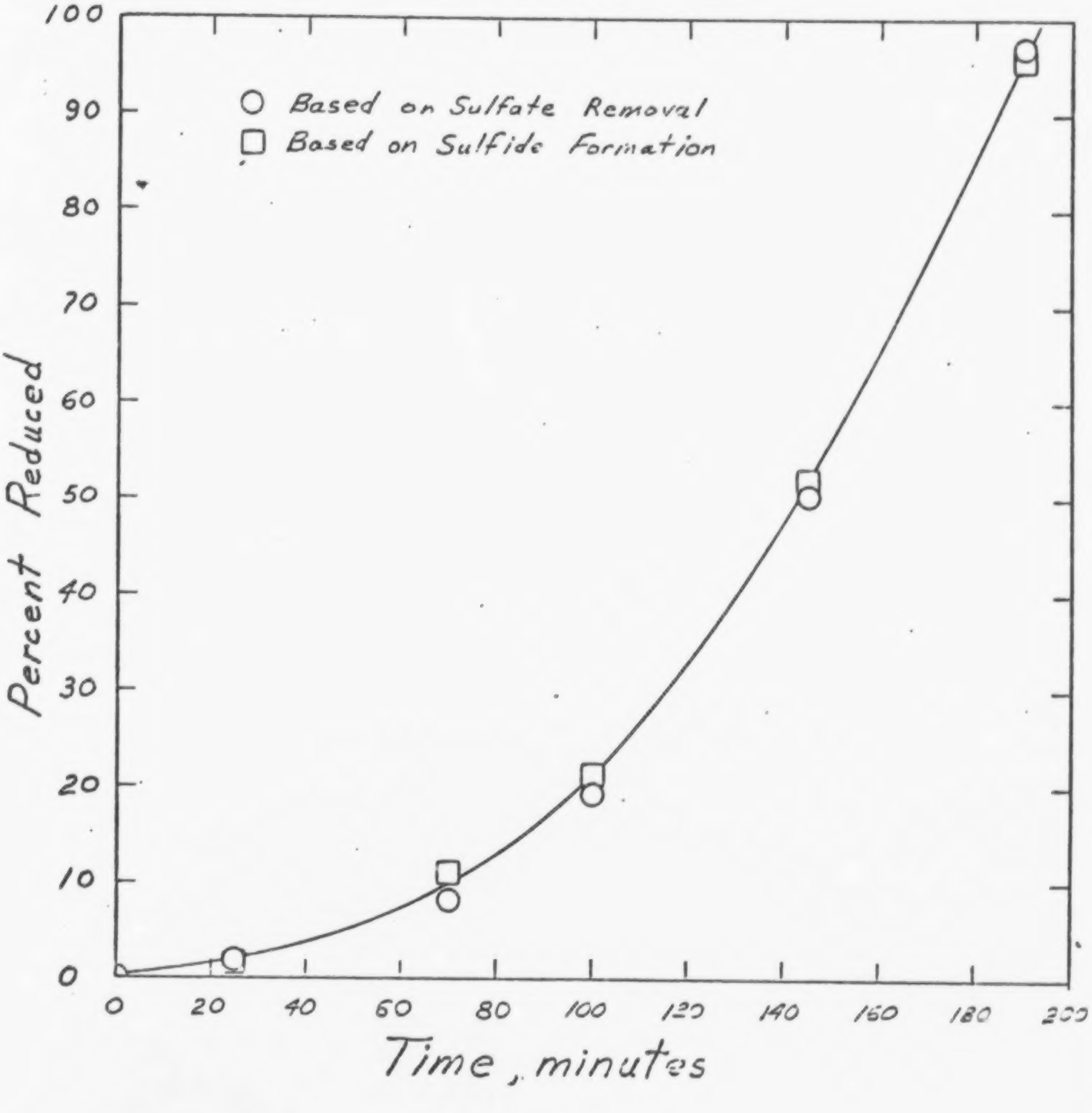


Figure 11. Reduction of Sulfate with Hydrogen in Graphite-Packed Contactor at 1110°F (600°C)

Examination of Figure 11 shows that complete reduction required nearly 200 minutes. This was much longer than the previous tests, done under nearly identical conditions but with carbon steel packing material; they required only one-third as much time. This suggested strongly that the iron in the packing material had increased the reaction rates in the previous reduction tests.

The curve of Figure 11 is shown replotted in Figure 12, along with the corresponding curves for the first tests done with carbon steel packing. Note that there is a significant difference in the shape of the curves. The first tests all yielded sigmoidal curves, with short induction periods when the reaction rates (corresponding to the slopes of the curves) were increasing, followed by longer periods of constant and then decreasing rates. In contrast, the slope increased throughout the test when the graphite packing was used. This shows that although the reaction rate was very slow at first, it increased continuously and was proceeding rapidly at the end of the test.

The continuously-increasing reaction rate could be due to iron catalysis, with the iron coming from corrosion of the stainless steel contactor walls. The iron content of the melt samples supports this hypothesis. The iron content of each sample was determined colorimetrically; the results are listed in Table 13, and plotted as a function of time in Figure 13.

Examination of Figure 13 shows that the concentration of iron in the melt increased as the test progressed, and there appears to be a relationship between iron content and reduction rate. The test results thus indicate that iron speeds up the reduction of sulfate by hydrogen. Hence, it

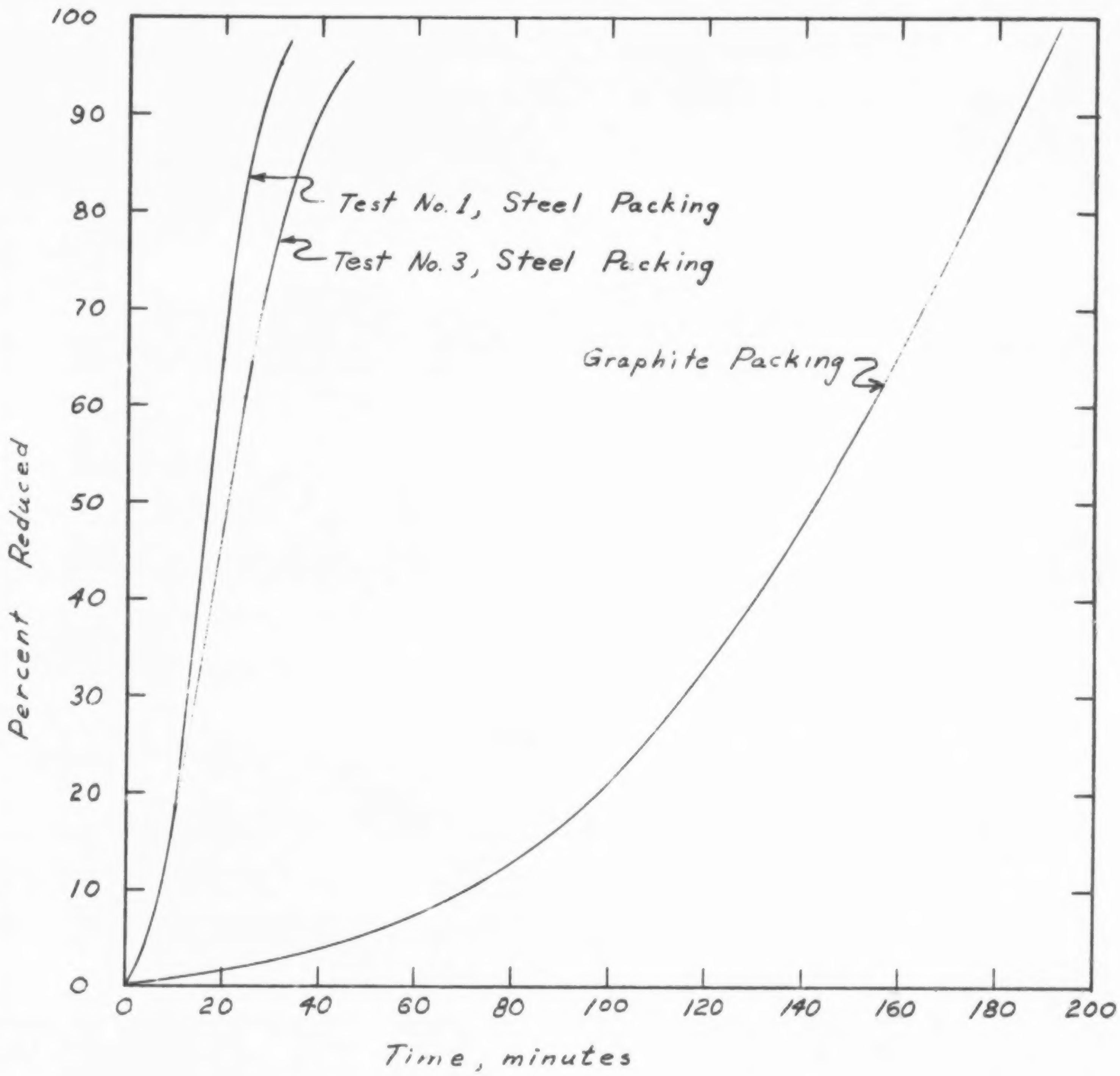


Figure 12. Comparison of Results of Reduction Tests at 1110°F (600°C)

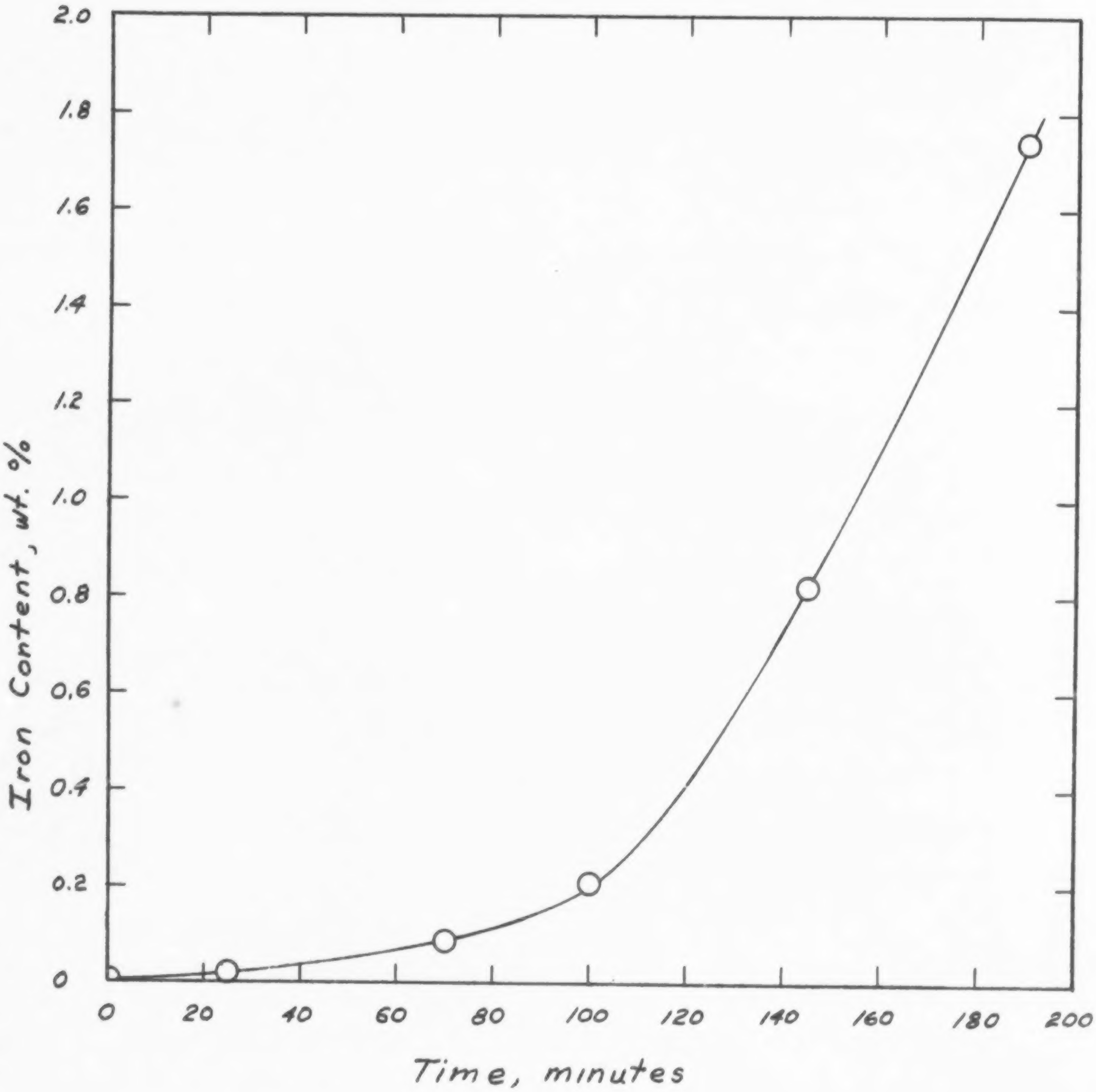


Figure 13. Iron Content of Melt Samples

TABLE 13

IRON CONTENT OF MELT SAMPLES

Time (min)	Iron Content (wt %)
0	0
25	0.02
70	0.09
100	0.21
145	0.82
190	1.74

may be possible to obtain significantly faster reduction rates by using the iron as a catalyst in a more effective way, or by using an even better catalyst. To investigate this, a systematic study of catalyzed reduction rates was carried out. This study is reported in Section 3-c below. First, the results of reduction tests with carbon monoxide and a mixture of carbon monoxide and hydrogen in steel-packed contactors are described.

(2) Carbon Monoxide Reduction Tests. The same rotating packed-bed contactors and test techniques were used to study reduction rates with carbon monoxide. Two tests were performed, with the experimental conditions as listed in Table 14.

TABLE 14

EXPERIMENTAL CONDITIONS, CO REDUCTION TESTS

	First Test	Second Test
Starting Material	22.3 wt % M_2SO_4 in 323.5 grams melt	24.5 wt % M_2SO_4 in ~ 300 grams melt
Temperature	1170°F (630°C)	
Pressure	1 atm	
CO Flow Rate	1 ℓ/min	
Packing	Clean carbon steel screws	

The reduction of sulfate with carbon monoxide should yield sulfide and carbon dioxide, according to reaction 8. To monitor the reaction rate, salt samples were taken periodically and analyzed for sulfate and sulfide concentration, and the amount of carbon dioxide evolved during the first test was measured by collecting it in an ascarite absorber. The exit gas compositions were also monitored periodically with a gas chromatograph, both to determine the relative amounts of carbon monoxide and carbon dioxide present and also to determine whether any other gases such as carbonyl sulfide, carbon disulfide, or hydrogen sulfide were being evolved. None of these other gases were found, indicating that complicating side reactions did not proceed to any extent. The exit gas was approximately 93% CO and 7% CO_2 during both tests.

The results of the first test are listed in Table 15.

TABLE 15

FIRST TEST - CARBON MONOXIDE REDUCTION OF SULFATE AT 1170°F (630°C)

Time (min)	Sample Composition (wt %)			CO_2 (grams)	Percent Completion Based On:		
	M_2CO_3	M_2SO_4	M_2S		M_2SO_4 Removal	M_2S Formation	CO_2 Evolution
0	78.3	22.3	0	0	0	0	0
15	77.7	—	0.3	1.6	—	2.3	1.7
45	78.5	19.8	0.7	5.4	11.2	5.4	5.8
75	81.8	17.6	0.7	9.9	21.1	5.3	10.6
115	86.8	12.7	1.1	18.0	43.0	8.4	19.3
160	90.0	6.8	1.3	28.9	69.5	9.9	31.0
260	98.8	0.2	2.1	45.5	99.0	16.0	48.7
100% Red'n	86.9	0	13.1	93.4			

The rate of the reduction reaction can be calculated from either (1) the amount of sulfate removed, (2) the amount of sulfide formed, or (3) the amount of carbon dioxide evolved. Values of these parameters from the salt sample analyses and carbon dioxide measurements were used to calculate the percent completion of the reduction; these data are listed in the last three columns of the table. Also, the percent completion based on sulfate removal is shown as a function of time in Figure 14.

The second test was run for only 2 hours, and no carbon dioxide measurements were taken. The results of this test are listed in Table 16, and the percent completion based on sulfate removal is also plotted in Figure 14.

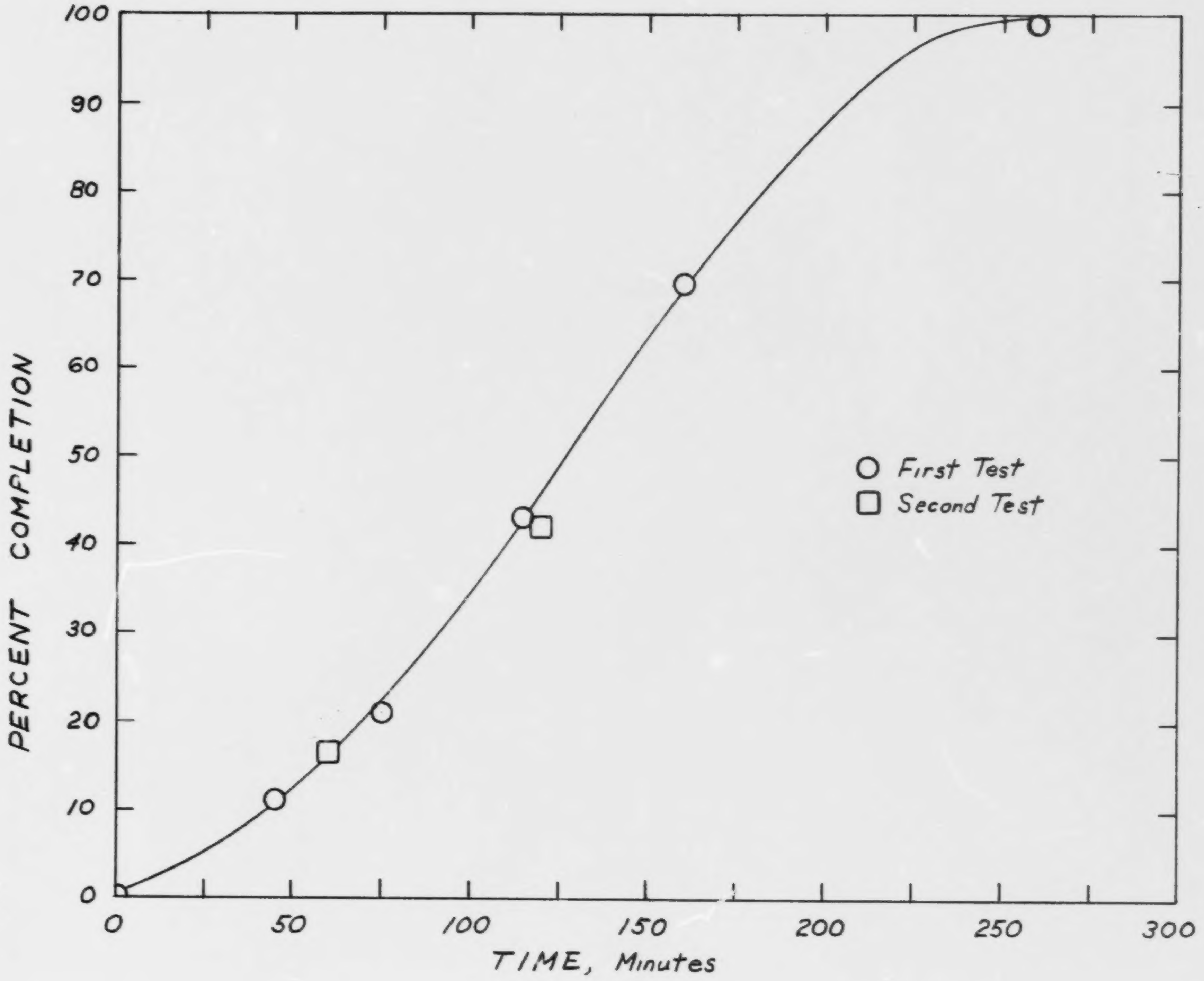


Figure 14. Reduction of Sulfate with Carbon Monoxide

TABLE 16

SECOND TEST - CARBON MONOXIDE REDUCTION OF SULFATE AT 1170°F (630°C)

Time (min)	Sample Composition (wt %)			Percent Completion Based On:	
	M_2CO_3	M_2SO_4	M_2S	M_2SO_4 Removal	M_2S Formation
0	77.7	24.5	0.1	0	0
60	78.8	20.5	0.6	16.3	3.5
120	85.7	14.2	1.2	42.0	7.7
100% Red'n	85.7	0	14.3	100	100

Examination of Figure 14 shows that the reduction rate based on sulfate removal was the same for the first 120 minutes of both tests, and that all of the sulfate was removed from the melt in about 260 minutes. This is more than 5 times as long as the 50 minutes required for the hydrogen reductions at 1110°F. Carbon monoxide is thus evidently much less effective than hydrogen as a reducing agent under the test conditions.

The data of Tables 15 and 16 also show that much of the sulfide and carbon dioxide which should have been produced in the tests was not found. The sulfide concentration of each salt sample was always less than half as great as it should have been if the sulfate was being reduced according to reaction 8, and only 16% of the theoretical amount of sulfide was found at the end of the first test. Also, only half of the theoretical amount of carbon dioxide was recovered in the first test.

The missing sulfide appeared to be in a sulfide-rich layer of salt immobilized on the carbon steel machine screws used for contactor packing. When the contactor was opened and emptied out after each test, the screws were found to be coated with a thick layer of dark grey material. Analysis of this material after the second test showed that it contained approximately 10% sulfide and only about 1% sulfate, compared to 1.2% sulfide and 14.2% sulfate for the corresponding melt.

It is also likely that the iron in the packing material reduced part of the sulfate to sulfide, just as in the hydrogen reduction test. This would also help account for the missing carbon dioxide, since no carbon dioxide is given off in the iron reduction (reaction 11).

Immobilization of the sulfide on the packing material could cause a problem in a continuous reduction process, where the sulfide must remain in the mobile melt phase and flow out of the reducer and into a regenerator. However, a corrosion-resistant packing material should eliminate this problem. If a catalyst material is used, then, it should of course be introduced in some other form, rather than as corrosion products from the packing.

(3) Reductions with a Mixture of Hydrogen and Carbon Monoxide. Reduction tests were performed with a mixture of hydrogen and carbon monoxide, in order to estimate reduction rates which can be expected using producer gas. A typical producer gas will contain nitrogen, carbon dioxide, and water as well as hydrogen and carbon monoxide, approximately in the proportions shown in Table 17. Of these constituents, the nitrogen is inert and will act only as a diluent to the hydrogen and carbon monoxide, the only gases which participate in the reduction

reactions. The carbon dioxide and water will not reduce sulfate or sulfite, but they may react with sulfide to regenerate carbonate and liberate hydrogen sulfide. While this reaction is not undesirable, its occurrence would remove sulfide and hence make it difficult to accurately measure the reduction reaction rate. For these reasons, mixtures containing only equal volumes of hydrogen and carbon monoxide were used in the reduction tests, where emphasis was on measuring reduction rates.

TABLE 17

TYPICAL PRODUCER GAS COMPOSITION(1)

	H_2	CO	CO_2	H_2O	N_2
Volume %	15	22	10	5	48

Two tests were performed, using the same equipment and procedure as was employed for the hydrogen and carbon monoxide test. However, preconditioned packing (i.e. machine screws used in a previous reduction test) was used in both cases. The experimental conditions were as listed in Table 18.

TABLE 18

EXPERIMENTAL CONDITIONS, CO-H_2 REDUCTION TESTS

	First Test	Second Test
Starting Material	21.6% M_2SO_4 plus 1.3% M_2S in carbonate melt	18.8% M_2SO_4 plus 4.6% M_2S in carbonate melt
Temperature	1170°F (630°C)	
Pressure	1 atm	
CO Flow Rate	1 ℓ/min	
H_2 Flow Rate	1 ℓ/min	
Packing	Conditioned carbon steel screws	

The two tests differed only in the composition of the starting material, and more particularly in the amount of sulfide initially present. (This initial sulfide was introduced as material stuck to the uncleaned reactor packing.) As in the carbon monoxide tests, the reaction rate was measured periodically by obtaining melt samples and analyzing them for sulfate and sulfide content. The exit gas compositions were also monitored with the gas chromatograph, but the carbon dioxide evolved was not collected.

The results of the salt sample analyses for the two tests are listed in Tables 19 and 20, and the percent completion based on sulfate removal is shown for each test in Figure 15.

TABLE 19

FIRST TEST - REDUCTION OF SULFATE WITH CO-H_2 MIXTURE AT 1170°F (630°C)

Time (min)	Sample Composition (wt %)			Percent Completion Based On:	
	M_2CO_3	M_2SO_4	M_2S	M_2SO_4 Removal	M_2S Formation
0	80.2	21.6	1.3	0	0
20	84.3	19.0	2.3	12.0	8.1
40	80.9	15.8	4.2	26.8	23.4
60	84.7	10.2	6.1	52.7	38.7
80	91.5	1.8	8.9	91.6	61.3
100% Red'n	86.3	0	13.7	100	100

TABLE 20

SECOND TEST - REDUCTION OF SULFATE WITH CO-H_2 MIXTURE AT 1170°F (630°C)

Time (min)	Sample Composition (wt %)			Percent Completion Based On:	
	M_2CO_3	M_2SO_4	M_2S	M_2SO_4 Removal	M_2S Formation
0	72.1	18.8	4.6	0	0
20	73.2	13.5	6.8	28.2	17.9
40	81.0	3.3	10.5	82.5	48.0
60	78.0	1.9	10.7	89.9	49.6
80	84.1	0.6	9.1	96.8	36.6
100% Red'n	83.1	0	16.9	100	100

The data of Figure 15 show that the sulfate was removed from both melts in about the same time, approximately 90 minutes, but that the initial reduction rate was much faster in the second test than it was in the first. One possible explanation for this is that the iron packing may have had different initial catalytic activity in the two tests.

Comparison of Figure 15 with Figure 14 and with the hydrogen reduction data of Figures 6 and 7 shows that the CO-H_2 gas mixture reduced the sulfate more rapidly than pure carbon monoxide but slightly slower than pure hydrogen. This indicates that the reaction proceeds with the two gases independently reducing the sulfate. This conclusion is further borne out by the results of the exit gas analyses, which showed that approximately 6 times as much water as carbon dioxide was evolved. Nearly 60% of the

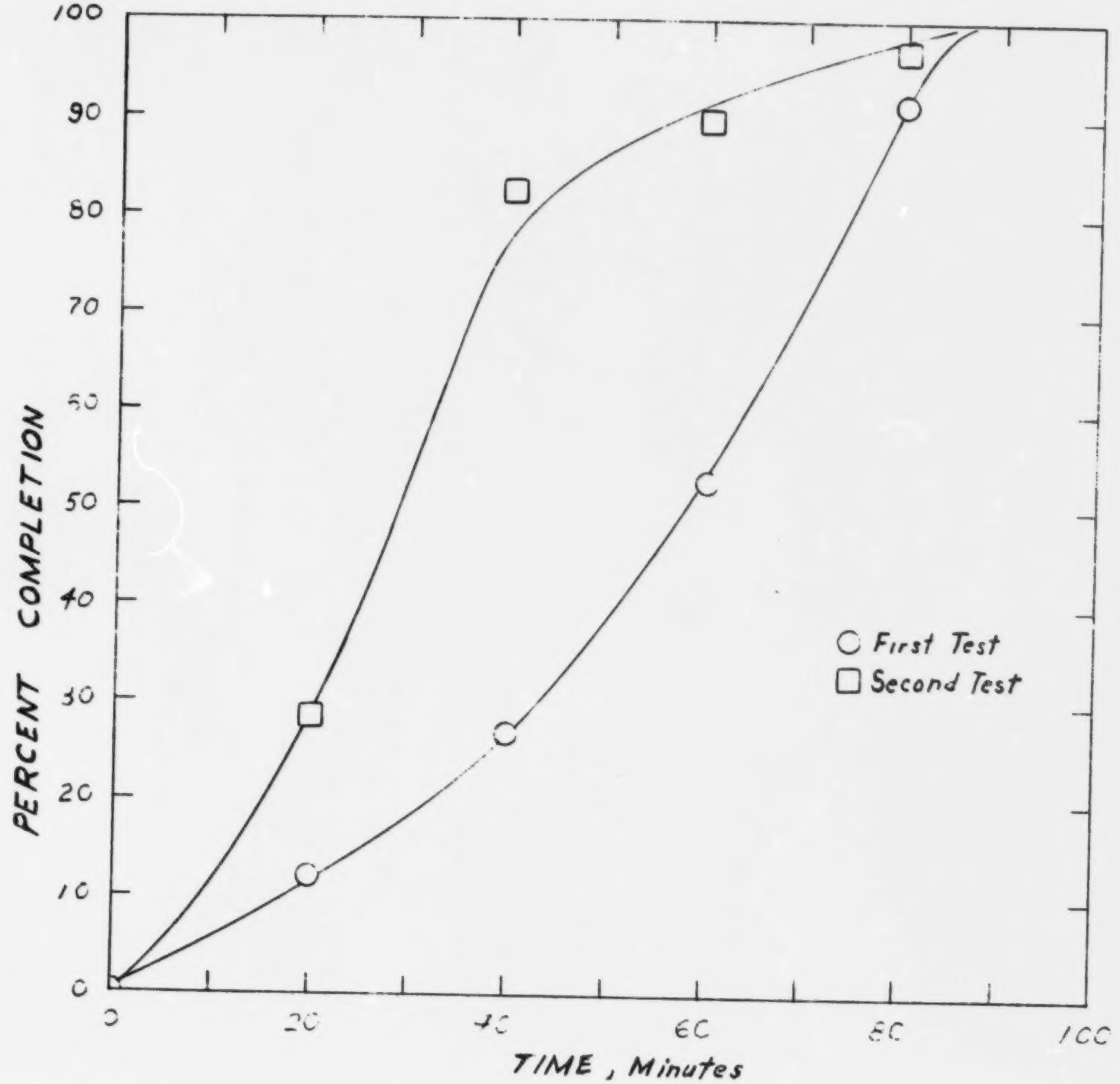


Figure 15. Reduction of Sulfate with CO-H_2 Mixture

hydrogen reacted, but only about 10% of the carbon monoxide reacted. Thus, it appears that hydrogen-rich gas streams will be the best reducing agents, and that it will be difficult to utilize all of the carbon monoxide in mixtures of the two gases. However, more definitive results will have to come from future countercurrent reduction tests.

The data of Tables 19 and 20 show that a larger fraction of the theoretical sulfide was found in the melts than was the case for the carbon monoxide tests. However, about 40% of the sulfide from the first test and 60% from the second test were still missing and apparently immobilized on the packing, even though preconditioned packing material was used.

It should be noted that if the iron in the packing acts as a reducing catalyst, then it evidently does not lose its effectiveness when coated with sulfide. This is indicated by the rapid initial reduction rate achieved with pre-coated packing in the second test.

The rotating packed bed contactor is an effective device for studying reduction rates, because it makes it possible to achieve rapid mass transfer between the melt and gas phases. However, it is different from a countercurrent packed bed contactor in that it does not have fresh salt feed material passing through it continuously, but instead always contains the same batch of salt. Because of this, reaction rates, yields, and efficiencies must be studied in a bench-scale countercurrent reduction contactor before the performance of continuous process units can be predicted.

The effect of iron and other possible catalysts on reaction rate also had to be determined. Tests performed to do this are described in the following section.

c. Catalyzed Reduction Tests

(1) Method. The results of the reduction tests described above indicated that corrosion products from stainless and/or carbon steels were taking part in the reduction reaction, and probably increasing the reaction rate. This raised the possibility of enhancing the reaction rate still more, by using a catalyst under controlled conditions. To do this, a study was necessary to determine the best catalyst and the conditions required for its maximum effectiveness. Such a study is being carried out, with a systematic series of tests to investigate the effectiveness of various compounds as catalysts.

In these tests, it was necessary to prevent any interference from extraneous corrosion products. Because of this, the test contactors were constructed of graphite, so that only carbon came into contact with the melts. This necessitated using bubbler-type contactors, i.e., graphite crucibles to contain the melts and graphite tubes to introduce the reducing gas. The graphite crucibles were sealed within steel capsules, so that the gases which bubbled through the melts could be collected and analyzed, but no metal was allowed to come in contact with the melts.

In this test program, control tests were first performed to measure the uncatalyzed reduction rate in the graphite bubbler contactor. Similar tests were then done with known amounts of iron or other suspected catalyst introduced into the melt, and the reduction rates compared with the control rate. Iron and iron salts were studied first, and then other transition metal salts, since these had been reported by other workers(2,3,4) to be effective in reducing solid sodium sulfate.

The first series of nine tests was done at 1110°F (600°C) using hydrogen as the reducing agent, at a flow rate of 1.4 ℓ/min. In all but the control tests, 0.14 moles of catalyst were used, and the melts were all made up to contain the same amount of sulfate (about 25 wt % sulfate as M_2SO_4). About 320 grams of melt were used in each test. The catalysts studied in these tests are listed in Table 21.

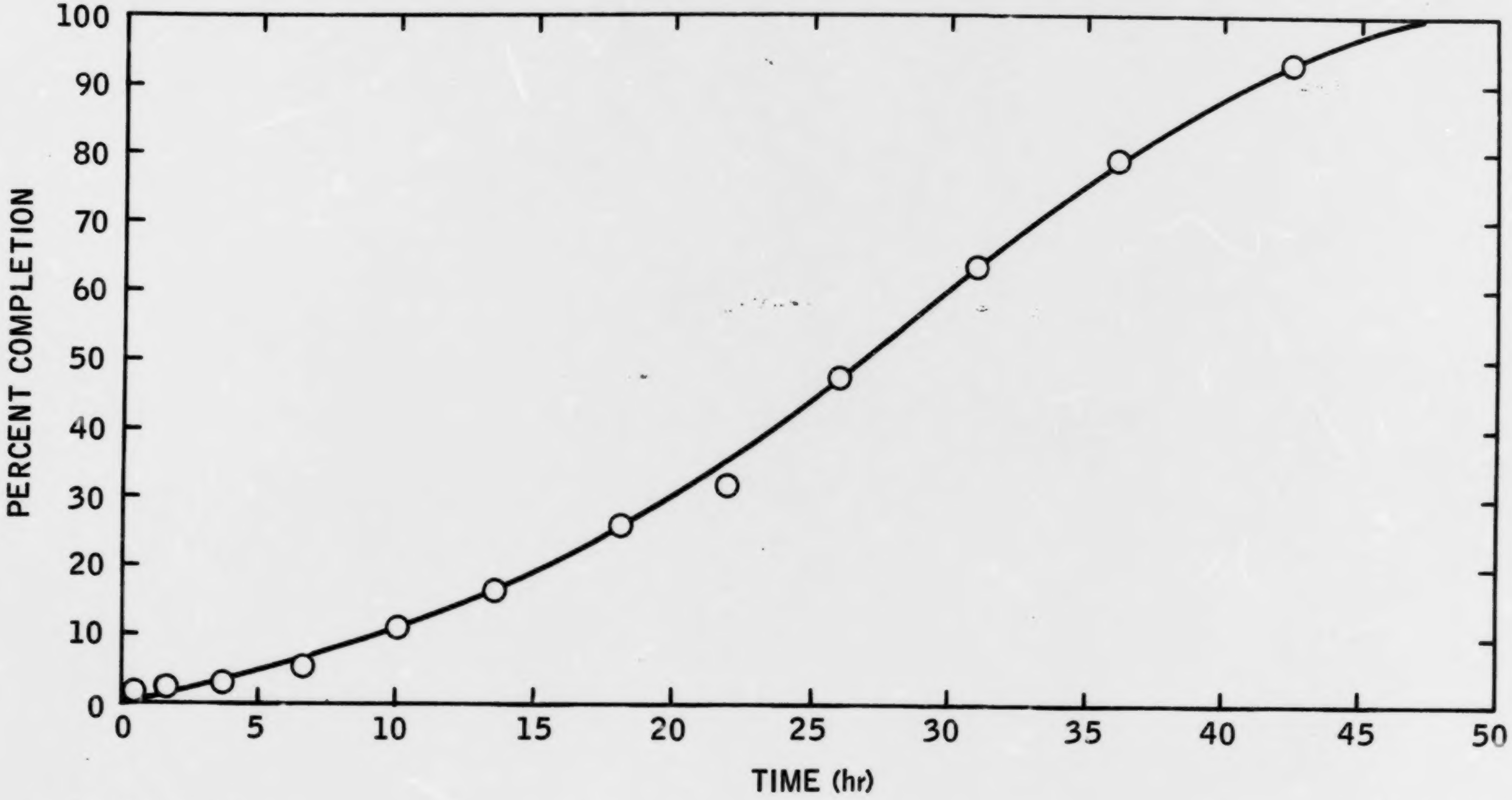
TABLE 21

CATALYSTS STUDIED WITH HYDROGEN
AT 1110°F (600°C)

Test Number	Catalyst
C-1	None (control)
C-2	$FeSO_4$
C-3	Fe
C-4	FeS
C-5	$SnSO_4$
C-6	Cr_2O_3
C-7	$MnSO_4$
C-8	$NiSO_4$
C-9	$CuSO_4$

The water evolved during each test was collected in a magnesium perchlorate absorber. This was weighed periodically, each time a melt sample was collected. The melt samples were analyzed for sulfate, sulfite, sulfide, and carbonate.

(2) Control Test at 1110°F. The results of the control test measurements are listed in Table 22. The fractional amount of sulfate reduced was calculated from the sulfate content of each sample. These values (the percent completion) are also listed in the table, and shown plotted as a function of time in Figure 16.



7-17-68 UNCL

7732-4012

Figure 16. Uncatalyzed (Control) Reduction Test at 1110°F (600°C)

TABLE 22

RESULTS OF CONTROL TEST WITH HYDROGEN AT 1110°F
(Test C-1; No Catalyst)

Time (hr)	Sample Composition (wt %)			Water (g)	Percent Completion
	M_2CO_3	M_2SO_4	M_2S		
0	75.2	25.4	0	0	0
1-1/2	74.6	25.0	0.3	0.6	1.6
3-1/2	76.2	24.7	0.5	1.4	2.8
6-1/2	75.6	24.0	1.4	2.8	5.5
10	76.8	22.7	2.0	4.7	10.6
13-1/2	75.6	21.4	3.2	7.0	15.7
18-1/4	76.9	18.8	5.0	10.5	26.0
22	76.9	17.0	6.4	13.9	31.5
26	76.3	13.5	9.2	18.2	46.9
31	76.3	9.5	11.5	23.5	62.6
36	77.8	5.4	15.8	28.5	78.7
42-1/2	76.9	1.7	17.3	32.8	93.3
Completion	84.7	0	15.3	43.0	100.0

Extrapolation of the curve of Figure 16 shows that the reduction would have required about 47 hours for completion. This was very slow, probably due to the relatively poor gas-liquid mass transfer in the bubbler-type contactor as well as to the lack of any catalyst. However, the results form an excellent basis with which to compare the other test results, which differed only in the presence of the different catalysts.

It should be noted that whereas 40 grams of water should have been evolved when the reduction was 93.3% complete, only 32.8 grams (82%) were actually found. Less water would have been evolved if part of the reduction was due to reaction with the graphite crucible or bubbler, but it is doubtful if this occurred to any significant extent due to the relatively low test temperature. The missing water may have remained dissolved in the melt, or it may have been absorbed by the graphite in the apparatus. It is probably significant, however, that considerably less water was missing than was the case when the reductions were done in the steel-packed rotating contactors, where part of the reduction was evidently due to reaction with the iron.

It also should be noted that the sulfide content of the last sample was 121% of the 14.3% which should have been present at that time. Also, the carbonate content was only 91% of the 84% which should have been present. This difference may be due to analytical inaccuracy and/or poor sampling technique; it is being investigated further.

(3) Iron Tests at 1110°F. The results of the three iron catalyst tests are listed in Table 23, and the percent completion values are also shown plotted versus time in Figure 17.

A comparison of the results with those for the control test indicates that the presence of iron definitely increased the reaction rate, reducing the time required for complete reduction by a factor of from 4 (for iron metal) to 7 (for ferrous sulfide). The most rapid reduction (with ferrous sulfide) required 7 hours for completion, much longer than the 1 hour required in the steel-packed rotating contactor tests at the same temperature and hydrogen flow rate. However, it is expected that the slow

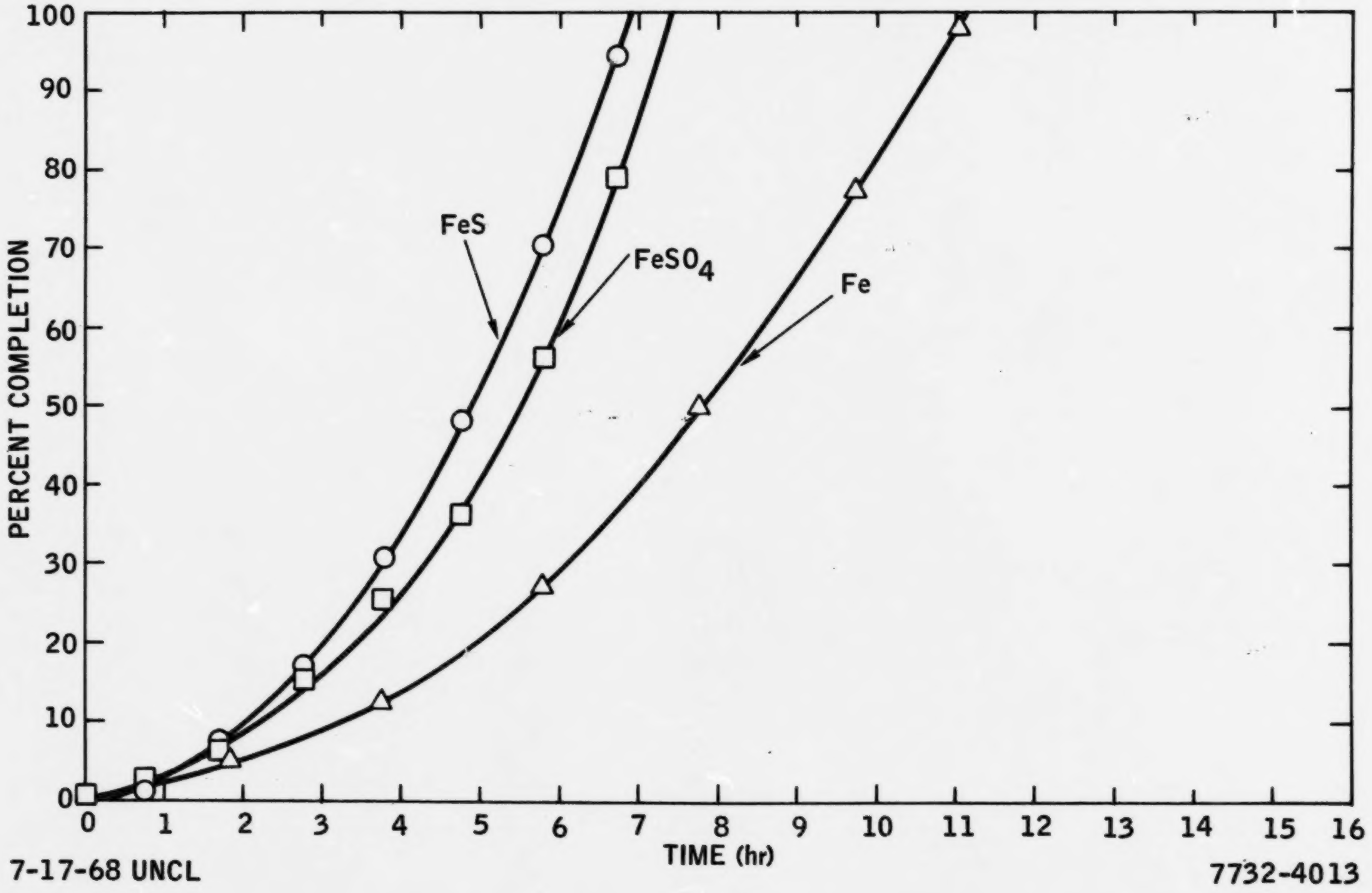


Figure 17. Iron Catalyst Test Results

TABLE 23

RESULTS OF IRON CATALYST TESTS AT 1110°F
(Tests C-2, C-3, and C-4)

Catalyst	Time (hr)	Sample Composition (wt %)			Water (g)	Percent Completion
		M_2CO_3	M_2SO_4	M_2S		
$FeSO_4$	0	74.5	25.0	0.1	0	0
	3/4	76.0	24.3	0.6	1.1	2.8
	1-3/4	71.7	23.3	0.9	2.7	6.8
	2-3/4	67.0	21.1	1.9	5.1	15.6
	3-3/4	70.2	18.6	3.5	8.8	25.6
	4-3/4	67.3	15.9	5.6	13.9	36.4
	5-3/4	76.2	11.3	9.2	16.9	54.8
	6-3/4	78.5	5.2	15.8	24.4	79.2
	8	73.5	0.1	17.5	32.7	99.6
	Completion	85	0	15.0	43.0	100
Fe	0	77.1	26.3	0	0	0
	3/4	78.9	25.9	0.2	0.4	1.5
	1-3/4	76.5	25.0	0.6	1.2	4.9
	3-3/4	75.5	23.0	1.2	2.7	12.5
	5-3/4	74.0	19.2	4.1	7.8	27.0
	7-3/4	75.2	13.2	8.0	15.7	49.8
	9-3/4	77.7	5.8	13.4	22.7	77.6
	11	80.5	0.4	17.3	28.5	98.5
	12	78.6	0	18.2	30.0	100
	Completion	84.5	0	15.4	43.0	100
FeS	0	70.7	27.0	2.0	0	0
	3/4	72.8	26.8	2.1	1.1	0.7
	1-3/4	71.2	25.0	3.3	3.2	7.4
	2-3/4	68.6	22.5	6.0	6.2	16.7
	3-3/4	70.0	18.8	8.4	10.0	30.4
	4-3/4	71.3	13.9	11.6	15.0	48.5
	5-3/4	75.7	8.1	16.1	20.4	70.0
	8	77.2	0	23.4	28.3	100
	Completion	81.3	0	18.7	43.0	100

rate is largely due to the difference in gas-liquid mass transfer rates in the two contactors. All-graphite rotating packed bed contactor tests are planned to measure catalyzed reaction rates under flowing conditions, after the optimum test conditions and catalysts are determined from bubbler test results.

The reduction curves for the ferrous sulfide and ferrous sulfate tests are quite similar. The slightly longer induction time required for the ferrous sulfate melt could be due to an initial reduction of the ferrous sulfate to ferrous sulfide, or to the need for more time to convert the sulfate to its effective form than was required for the sulfide. At any rate, the two curves are essentially parallel after about 30% of the reduction was achieved. This indicates that these two iron compounds were about equally effective as catalysts.

The reduction rate achieved with pure iron was, in contrast, significantly slower than that achieved with either of the two iron compounds. This is probably due to the time required to convert the iron metal into its effective form. The iron was introduced in the form of iron powder. It was noted that the first 4 samples (at 0, 3/4, 1-3/4, and 3-3/4 hours) were magnetic, while the remaining samples were not. The iron thus reacted to form a non-magnetic compound rather slowly. Apparently this non-magnetic compound was a more effective catalyst, since the reaction rate appeared to increase continuously during the entire test.

As in the control test, there was less than the theoretical amount of water collected during each test, and more than the theoretical amount of sulfide was found.

(4) Tin Test at 1110°F. The results of the test with stannous sulfate are listed in Table 24 and plotted in Figure 18.

TABLE 24

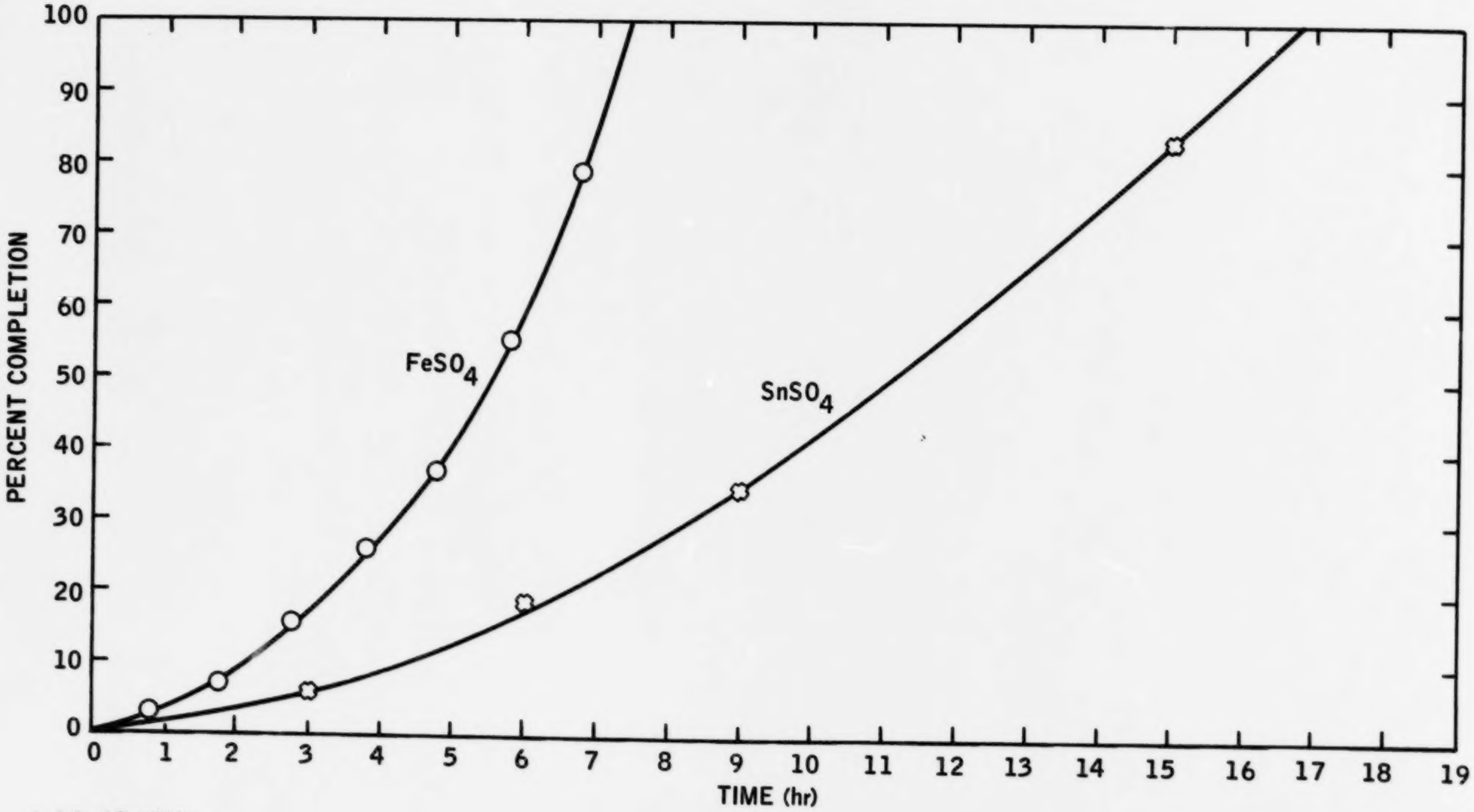
RESULTS OF TIN CATALYST TEST AT 1110°F (600°C)
(Test C-5; $SnSO_4$ Catalyst)

Time (hr)	Sample Composition (wt %)			Water (g)	Percent Completion
	M_2CO_3	M_2SO_4	M_2S		
0	73.8	24.2	0	0	0
3	70.2	22.9	0.1	4.1	5.4
6	70.9	19.7	0.2	8.8	18.6
9	74.2	15.9	5.2	14.6	34.3
15	74.2	4.0	11.6	29.2+*	83.5

*Some exit gas was lost

The curve for the ferrous sulfate reduction from Figure 17 is also replotted in Figure 18 for comparison. The results show that tin definitely increased the reduction rate over that of the control test, but that it was not as effective for this as was iron. The tin sulfate reduced the time for completion by a factor of 2.8 over that for the control test, while the iron sulfate reduced the time by a factor of 7.

(5) Reduction Mechanism. The remaining transition metals tested (chromium, manganese, nickel, and copper) had no measurable effect on the reduction rate. However, it was noted that the metals to the right of iron in the periodic table (nickel and copper) appeared to separate from the melt as metal particles, while those to the left of iron (chromium and manganese) remained in the melt but as insoluble particles, perhaps of the metal



7-17-68 UNCL

7732-4014

Figure 18. Comparison of Tin and Iron Catalysts

oxide. This suggested that iron might exist both as the element and as a compound under the test conditions. If this is so, then it is possible that the reduction reaction mechanism involves both forms of iron, i.e. the reduction may proceed according to the reactions

$$4H_2 + Fe_3O_4 \rightarrow 4H_2O + 3Fe \qquad (13)$$

$$3Fe + M_2SO_4 \rightarrow M_2S + Fe_3O_4 \qquad (14)$$

or, for some other metal X forming an oxide of the form X_nO_m,

$$mH_2 + X_nO_m \rightarrow mH_2O + nX \qquad (15)$$

$$nX + \frac{m}{4} M_2SO_4 \rightarrow \frac{m}{4} M_2S + X_nO_m. \qquad (16)$$

For such a mechanism to hold, the free energies of reactions 15 and 16 must both be favorable, i.e. negative. This criterion could then be used to examine other metal-metal oxide pairs for potential catalytic activity. For this, the free energies of reactions 15 and 16 have been estimated for several metals, and listed in Table 25.

Examination of this table shows that iron, tin, molybdenum, and germanium have negative free energies for both reactions, and hance may be catalytically active. This was, in fact, what led to the choice of tin for one of the tests; molybdenum and germanium will be tried in the future, to further test the theory. The tabulated data also tend to explain the findings for copper, nickel, manganese, and chromium. The free energy data for copper and nickel indicate that the metal oxide would be reduced to metal, as was found, but that the metal would not reduce sulfate. For manganese and chromium, in contrast, the data indicate that the metal oxides would not be reduced, and no metal was ever observed in the melt samples during tests with these two.

TABLE 25

FREE ENERGIES OF REACTIONS 15 AND 16

Metal, X	Metal Oxide, X_nO_m	ΔF Reaction 15	ΔF Reaction 16
Fe	Fe_3O_4	+0.2	-27.7
Fe	Fe_2O_3	-2.0	-19.1
Fe	FeO	-1.8	-29.4
Sn	SnO_2	-0.9	-24.1
Cr	Cr_2O_3	+22.3	-116.1
Mn	MnO	+28.0	-138.9
Cu	CuO	-29.5	+95.8
Ni	NiO	-10.1	+12.2
Co	CoO	-9.5	+10.4
Cd	CdO	-8.3	+6.4
Sb	Sb_2O_3	-12.1	+20.2
Os	OsO_4	-41.1	+137.6
Mo	MoO_2	-0.8	-24.6
Mo	MoO_3	-6.7	-1.5
Ge	GeO_2	-4.8	-8.0
In	In_2O_3	+4.2	-44.9

The mechanism of reactions 15 and 16 would also work for elements in two different oxidation states, as well as for metals and their oxides. A survey of as many catalysts as possible will be made, and those having favorable thermodynamic data will be tested for catalytic activity.

(6) Effect of Temperature. To study the effect of temperature on the catalyzed reduction rate, two tests were performed that were similar to the ferrous sulfate test at 1110°F (C-2) in all respects except that the temperatures were 1200°F (650°C) and 1290°F (700°C). A control (uncatalyzed) test was also done at 1290°F for comparison. The results of these tests are tabulated in Table 26, and shown plotted in Figure 19 along with the results of the control and ferrous sulfate tests at 1110°F (600°C) for comparison.

The plots show that there is a significant increase in the catalyzed reaction rate as the temperature is raised from 600°C to 700°C. The average reduction rate during the period between 25% and 75% reduction has been tabulated for each curve of Figure 19 in Table 27.

TABLE 26

RESULTS OF TESTS AT 1200°F (650°C) AND 1290°F (700°C)

Catalyst and Temperature (°F)	Time (hr)	Sample Composition (wt %)			Water (g)	Percent Completion
		M_2CO_3	M_2SO_4	M_2S		
Control, 1290	0	80.0	26.3	0	0	0
	1	78.8	24.7	0.9	2.5	6.1
	2-1/4	76.0	23.1	2.1	5.9	12.2
	3-3/4	76.8	19.4	4.8	11.1	26.2
	5-1/4	78.0	14.6	7.7	17.6	44.5
	6-3/4	79.0	8.9	12.4	25.2	66.2
$FeSO_4$ 1200	0	75.5	26.1	0.1	0	0
	3/4	74.2	25.2	0.6	1.4	3.4
	1-3/4	69.3	23.3	2.2	4.6	7.3
	2-3/4	70.9	20.1	4.4	9.1	23.0
	3-1/2	72.0	16.2	6.9	13.9	37.9
	4-1/4	73.2	11.3	9.7	20.0	56.7
	4-3/4	73.4	7.2	13.4	24.6	72.4
	5-1/2	77.5	0.9	17.4	32.5	96.6
$FeSO_4$ 1290	0	74.9	26.2	0	0	0
	1	72.4	23.0	2.1	4.1	12.2
	1-3/4	71.0	18.7	5.3	10.0	28.6
	2-1/4	72.0	14.7	9.0	13.8+*	43.9
	2-3/4	71.1	8.8	12.8	21.0+	66.4
	3-1/2	75.9	2.1	17.0	28.8+	92.0

*Some exit gas was lost

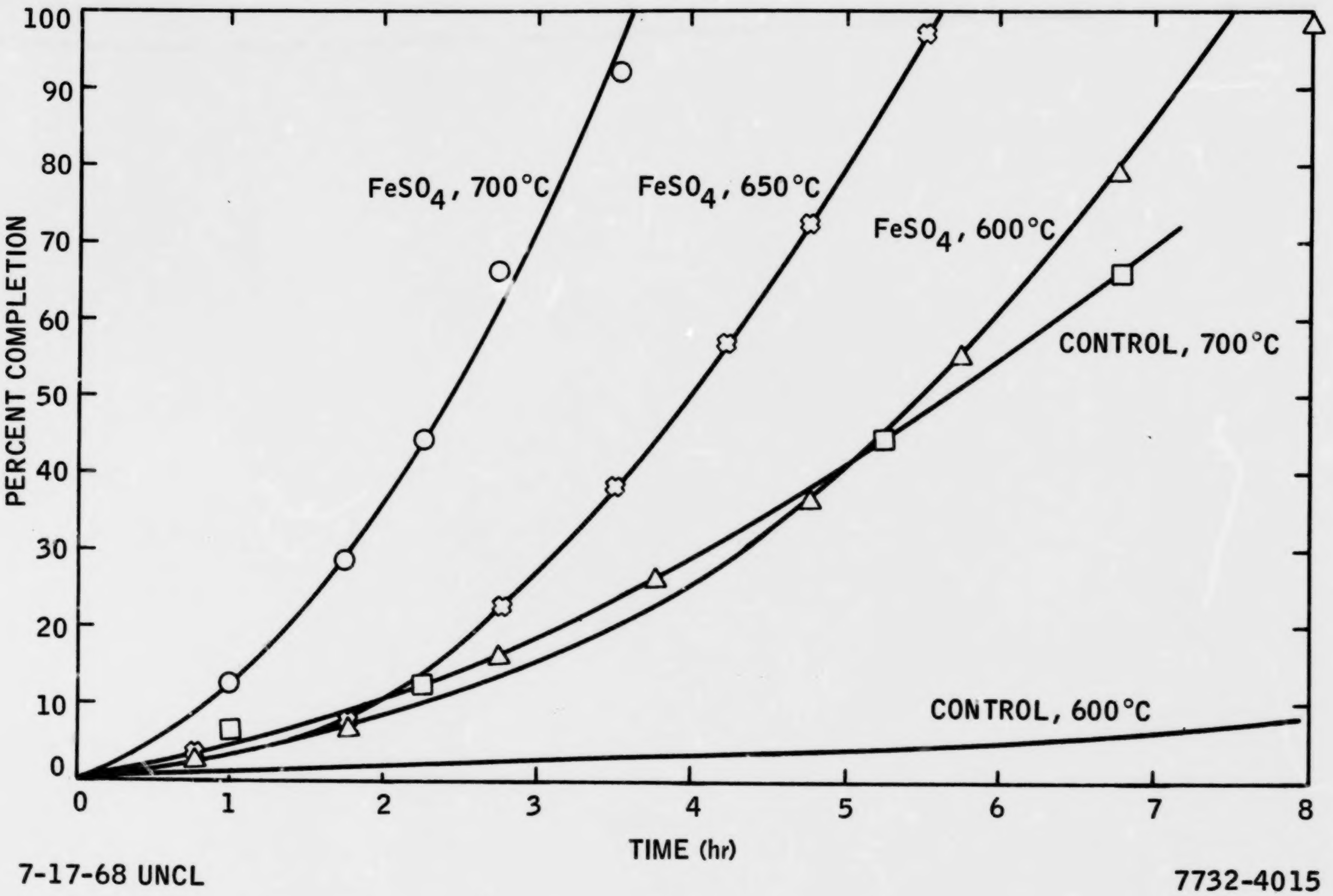


Figure 19. Effect of Temperature on Reduction Time

TABLE 27

AVERAGE REDUCTION RATES

Catalyst	Temperature (°C)	Average Rate (% per hour)
None	600	3.0
None	700	13.3
$FeSO_4$	600	17.5
$FeSO_4$	650	25.0
$FeSO_4$	700	38.1
$SnSO_4$	600	7.7

These data show that the uncatalyzed reduction rate increased by a factor of 4.5 between 600°C and 700°C, while the catalyzed rate increased by only a factor of 2.2 over the same temperature range. This difference is presumably due to the decrease in activation energy of the catalyzed reactions. The temperature effect for the rotating packed contactor reductions was reported in section 3-b above as approximately a factor of 5 increase between 600°C and 700°C. However, in these tests the corrosion product concentrations were not constant from test to test or even during any one test. Because of this, the factor of 2.2 increase per 100°C is probably more accurate.

(7) Carbon Monoxide Reduction. It is planned to study the effect of catalysts on the rate of reduction with carbon monoxide, as well as with hydrogen. To date, only an uncatalyzed control test has been done, at 1290°F (700°C). This test was done the same way the hydrogen control tests were done, in an identical all-graphite system. The carbon

dioxide evolved was collected in an ascarite absorber. The results are listed in Table 28 and plotted in Figure 20.

TABLE 28

RESULTS OF CARBON MONOXIDE REDUCTION AT 1290°F (700°C)
(Control Test; No Catalyst)

Time (hr)	Sample Composition (wt %)			CO_2 (g)	Percent Completion
	M_2CO_3	M_2SO_4	M_2S		
0	77.5	26.8	0	0	0
1	78.1	26.2	0.1	2.0	2.2
3-3/4	81.5	25.3	0.7	8.3	5.6
6-3/4	77.5	24.3	1.4	12.5+*	9.3
11-3/4	81.5	20.8	3.9	--*	25.4
21-1/2	86.5	0	20.0	--*	100.0

*Exit gas was lost

The results of the uncatalyzed hydrogen reduction at 1290°F (700°C) are also plotted in Figure 20 for comparison.

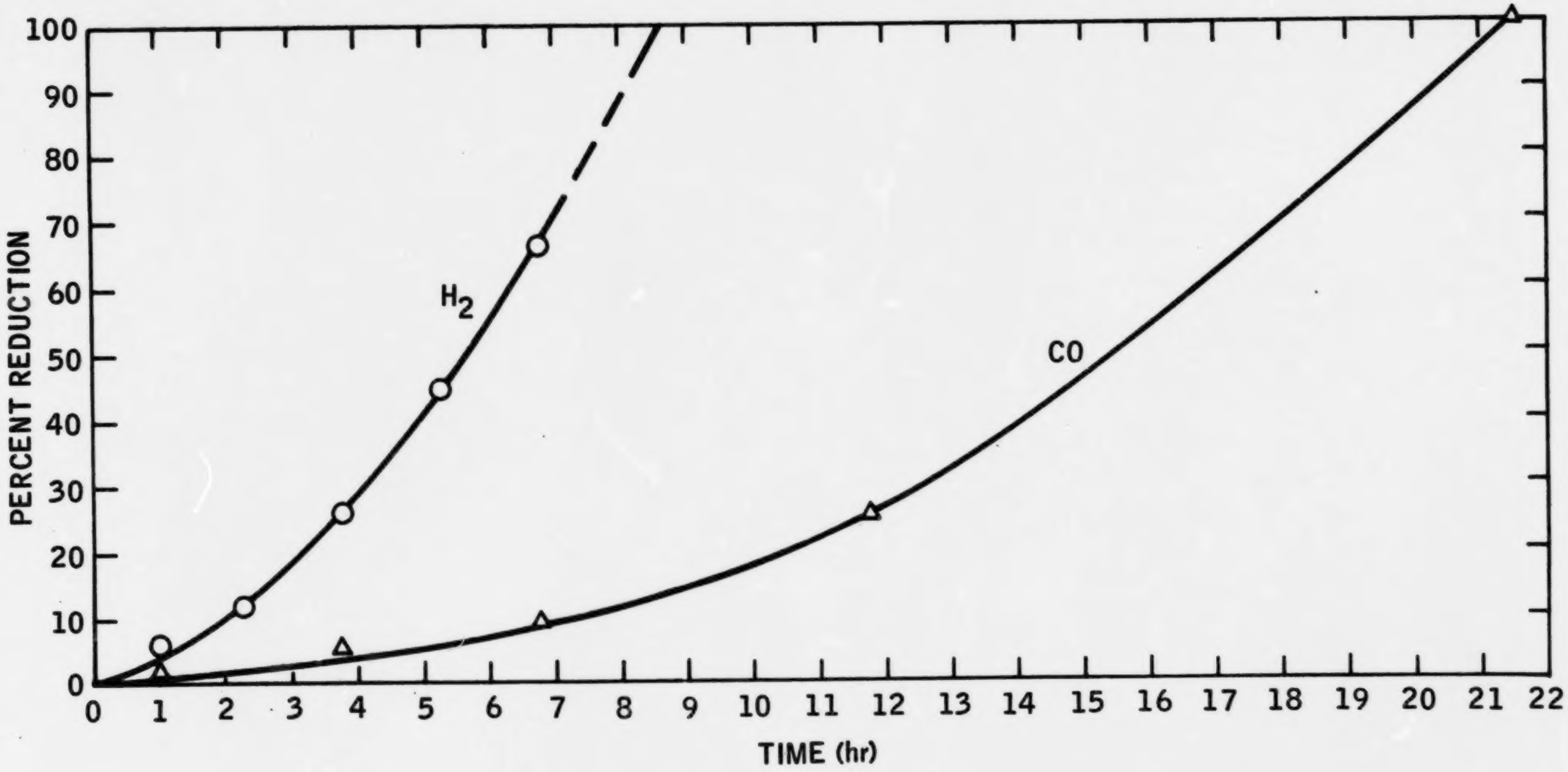
The curves indicate that at this temperature the complete reduction with carbon monoxide would require about 2-1/2 times as long as with hydrogen. This is more favorable than the factor of about 6 found from packed bed tests at 1110°F (600°C).

4. Regeneration Studies

The regeneration reaction is

$$M_2S + H_2O + CO_2 \rightarrow H_2S + M_2CO_3. \qquad (10)$$

In the regeneration process, the sulfide formed in the reduction step must



7-17-68 UNCL

7732-4016

Figure 20. Carbon Monoxide and Hydrogen Reductions at 1290°F (700°C)

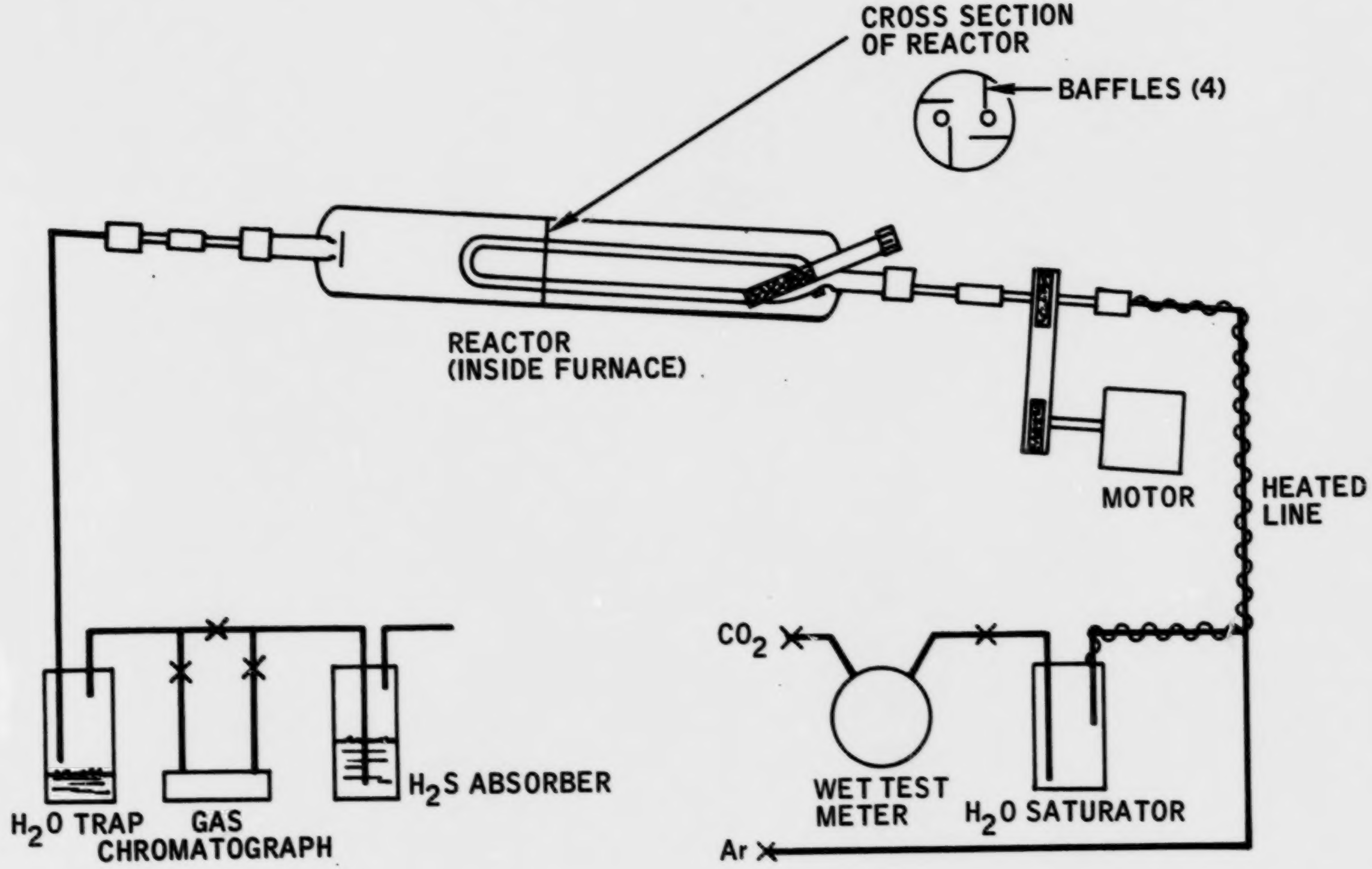
be converted into carbonate for recirculation to the absorber, and the sulfur must be recovered as hydrogen sulfide. The rate of conversion must be rapid and the yield of both carbonate and hydrogen sulfide must be high for the process to be successful. Both rate and yield have been studied experimentally, but emphasis has been placed on first determining conditions for high yields. The first tests were performed with synthetic melts of sulfide in carbonate. The more recent tests were done with melts actually formed during reduction tests.

a. Regeneration of Synthetic Melts

(1) Rotating Packed Bed Contactor Tests. Two experiments were performed to study the regeneration of synthetic sulfide-carbonate melts in rotating packed bed contactors. The experimental arrangement for these tests is shown in Figure 21. The contactor was similar to those used for reduction tests. It was made of type 347 stainless steel, and filled about 1/3 full of carbon steel machine screws, which provided a large surface area for contact between the gas phase (steam plus carbon dioxide) and the melt.

In the first test, the reactor void space was half filled with a carbonate-sulfide melt, made from anhydrous alkali metal carbonates and sodium sulfide. Sodium sulfide is quite hygroscopic, and normally occurs as $Na_2S \cdot 7H_2O$; the material used was dried and dehydrated as well as possible under vacuum at 200°C, but still contained some water.

The reactor containing the melt was purged with argon during the heat-up period, and a melt sample was taken when the temperature reached 840°F (450°C). Carbon dioxide saturated with water vapor at 80°C was then passed through the reactor for 45 min and another sample taken. The


CROSS SECTION
OF REACTOR
BAFFLES (4)
REACTOR
(INSIDE FURNACE)
MOTOR
HEATED
LINE
CO_2
WET TEST
METER
H_2O SATURATOR
Ar
H_2O TRAP
GAS
CHROMATOGRAPH
H_2S ABSORBER

7-17-68 UNCL

7732-4017

Figure 21. Rotating Reactor for Carbonate Regeneration

reactor was then cooled, opened, reheated to empty it of its contents, and the remaining melt was drained from the screws. Analysis of the melt samples at the start and end of the regeneration showed the initial concentration was 4.05% sulfide (as M_2S) and that this had been reduced to 0.3% sulfide (as M_2S). However, the hydrogen sulfide given off during the test contained only 7% of the total sulfur originally present. Most of the missing sulfur was found in a sulfide-rich layer of salt and corrosion products coating the machine screw packing material. A final sulfur balance showed the following:

Recovered as H_2S	7%
Adhering to Packing	88%
Remaining in Melt	5%

The results indicate that most of the sulfide reacted with the carbon steel packing material during the test, probably forming an iron sulfide, and that this iron sulfide was not reduced to hydrogen sulfide by the carbon dioxide-steam mixture. However, the sulfide content of the liquid melt was markedly reduced by the treatment.

A second test was performed, using the same contactor and the packing as it was after the first test. The results were quite similar; again the free melt sulfide concentration was reduced significantly but little of the sulfur was recovered as hydrogen sulfide. This indicated that the preconditioned iron packing continued to react with the sulfide in the melt. It thus became apparent that the tests would have to be done in systems with much less iron surface exposed to the melt. Since no corrosion-resistant packing materials were available, bubbler-type contactors were used. However, it was realized that the rate of regeneration probably could not be determined accurately with bubbler tests, because of poor gas-liquid mass transfer.

(2) The Bubbler Test. In this test, the sulfide-carbonate melt was contained in a type 347 stainless steel crucible, which was heated inside a quartz tube within an electric furnace. A diagram of the apparatus is shown in Figure 22.

The melt for this test was prepared in situ by bubbling hydrogen sulfide through a carbonate melt containing sodium hydroxide. This reaction was carried out at 930°F (500°C), and proved to be a rapid and convenient way to prepare carbonate-sulfide melts. However, the final sulfide content of the melt could not be controlled as closely as expected from the neutralization reaction

$$H_2S + 2NaOH \xrightarrow[(Li,Na,K)_2CO_3]{500°C} Na_2S + 2H_2O \qquad (17)$$

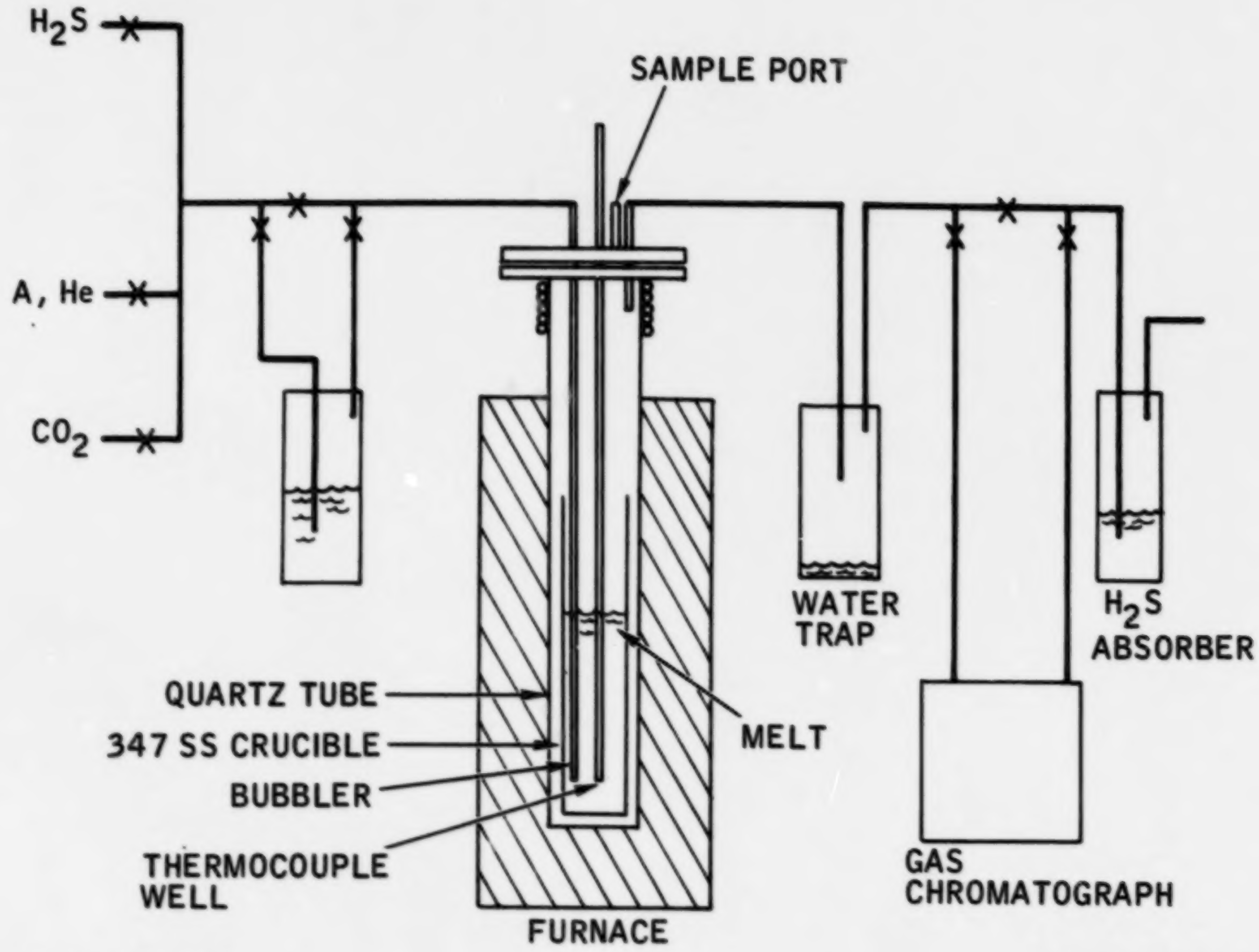
when excess hydrogen sulfide was used. The reaction, based on the final sulfide content of the melt, appeared to be in part

$$H_2S + NaOH \xrightarrow[(Li,Na,K)_2CO_3]{500°C} NaHS + H_2O. \qquad (18)$$

The recovered water of neutralization amounted to only about half of theoretical, based on equation 17 and the weight of sodium hydroxide. The carbonate-sulfite melt thus appeared able to retain water for some time at 500°C, as there was no indication of additional water loss from these melts during a 2 hour purge with argon after the hydrogen sulfide treatment.

Because it was expected that the melt contained water, dry carbon dioxide was passed through the melt first. This was done to determine if water was still retained in the melt at 930°F and also to convert any excess sodium hydroxide to sodium carbonate by the reaction

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O. \qquad (19)$$


H_2S
A, He
CO_2
SAMPLE PORT
QUARTZ TUBE
347 SS CRUCIBLE
BUBBLER
THERMOCOUPLE WELL
MELT
FURNACE
WATER TRAP
H_2S ABSORBER
GAS CHROMATOGRAPH

7-17-68 UNCL

7732-4007

Figure 22. Bubbler Reactor for Carbonate Regeneration

In either case, whether water of hydration or hydroxide was present, hydrogen sulfide was produced when the melt was treated with carbon dioxide. When carbon dioxide was bubbled through the melt, substantial quantities of hydrogen sulfide were evolved over a 30 min period, and then it continued to be produced at about 1/4 the initial rate during the next 60 min period. During this last period, carbonyl sulfide was observed in the exit gas in about the same concentration as the hydrogen sulfide. The sulfide content of the melt after the 90 min treatment with dry carbon dioxide had decreased from 25.1 to 16.8 wt %. At this time, carbon dioxide saturated with water was bubbled through the melt for 15 min, and the sulfide content decreased from 16.8 to 4.6 wt %. A further treatment with carbon dioxide saturated with water for about 20 min, reduced the sulfide content from 4.6 to 0.91 wt %. The test was then discontinued.

The gas chromatographic analysis of the exit gases during the two periods when carbon dioxide saturated with water was bubbled through the melt showed that substantial quantities of hydrogen sulfide were being evolved. At the same time, the gas chromatograph peak corresponding to carbonyl sulfide disappeared. The sulfur balance for this test showed that 81% of the sulfur was accounted for as hydrogen sulfide. The remainder was probably carbonyl sulfide and hydrogen sulfide lost from the exit gases during sampling and from the absorbing train. During the test, the bubblers in the aqueous sodium hydroxide solution plugged several times because of a build-up of sodium carbonate. During replacement of these bubblers, some exit gases escaped into the venting system.

The melt which remained in the reactor was almost completely reformed into pure carbonate.

These results indicated that good yields of carbonate and hydrogen sulfide could be obtained by regeneration with carbon dioxide and steam when there was not a lot of iron available to tie up the sulfur. However, the melt used may not represent very well the actual melts which will have to be regenerated. Because of this, regeneration tests were performed with the melts produced during the reduction tests described in section 3-c above.

b. Regeneration of Melts from Reduction Tests

The reduction tests described in section 3-c above produced melts which are probably very similar to those which will be regenerated in the actual process. Following seven of these reduction tests, the melts were regenerated in their original graphite crucibles. This was done by simply connecting the gas inlet and exit lines to the gas feed, collection, and sampling equipment used for regeneration (Fig. 22), cooling the melts to the regeneration temperature, and then bubbling the regenerating gases through the melts.

In all but one test, the regeneration was done in two steps. In the first step, dry carbon dioxide and helium were bubbled through the melt, without water vapor being added. This was then followed by the second step, in which the melt was treated with a water vapor-carbon dioxide-helium mixture. In one test (R7 below), the first step was omitted and the water vapor-carbon dioxide-helium mixture was used from the start. (The helium was used as a continuous purge, to keep the gas lines open.)

The dry carbon dioxide treatment of step 1 was used to investigate the ability of the (newly reduced) melts to absorb carbon dioxide. In all cases, the melts did absorb a significant amount of carbon dioxide, without emitting any hydrogen sulfide. This is in contrast to the regeneration of the synthetic sulfide melts, where the carbon dioxide generated hydrogen sulfide. It may indicate that the melts contain alkali metal oxides, perhaps formed during reduction by the reaction

$$M_2CO_3 \rightleftharpoons M_2O + CO_2. \tag{20}$$

The oxide would then absorb carbon dioxide (or water) during regeneration to reform the carbonate, or hydroxide which would later be converted to carbonate. This effect would increase the regeneration gas feed requirements, and also perhaps cause a delay in the emission of hydrogen sulfide. A quantitative study of this will be done in the future.

The regeneration temperature was kept at 930°F (500°C) for all seven tests, and when wet gases were used, they were formed by saturating the dry carbon dioxide with water at approximately 90°C. This yielded a mixture of about 70% water vapor and 30% carbon dioxide. The dry carbon dioxide flow rate was held constant during each test. The melts regenerated, carbon dioxide flow rates, and contact times are listed in Table 29.

TABLE 29

REGENERATION TEST CONDITIONS
930°F (500°C)

Test	Reduction Conditions		Regeneration Gas Flow Rates and Contact Times		
	Temp (°C)	Catalyst	Dry CO_2 Flow Rate (ml/min)	Dry CO_2 Contact Time (min)	Wet CO_2* Contact Time (min)
R1	600	None	300	10	148
R2	700	None	100	60	170
R3	600	$FeSO_4$	150	24	144
R4	600	Fe	150	60	150
R5	600	FeS	75	82	150
R6	600	$SnSO_4$	150	62	77
R7	700	$FeSO_4$	150	0	230

*Saturated at approximately 90°C, i.e. about 70% H_2O, 30% CO_2

Melt samples were taken periodically and analyzed. For tests R2 to R6, these samples were taken (1) at the beginning of the test, (2) at the end of the dry carbon dioxide contact period (step 1), and (3) at the end of the test. The melts from tests R1 and R7 were sampled only at the beginning and end of the test. Also, the depth of the melt pools in the crucibles were measured with the sample tubes, and used to estimate the amounts of melt present. These data are all listed in Table 30.

TABLE 30

MELT COMPOSITION DURING REGENERATION

Test	Sample*	Melt Composition (wt %)			Melt Volume (ml) (Estimated)
		M_2CO_3	M_2SO_4	M_2S	
R1	1	76.9	1.7	17.3	115
	3	97.6	1.7	0	103
R2	1	79.0	8.9	12.4	100
	2	81.0	8.9	11.3	117
	3	92.7	8.9	0.1	117
R3	1	73.5	0.1	17.5	-
	2	83.0	-	17.2	125
	3	101.2	-	0.2	81
R4	1	78.6	0	18.2	101
	2	86.7	0	13.5	122
	3	94.8	0	0.3	100
R5	1	77.2	0	23.4	69
	2	86.5	0	19.4	81
	3	101.1	0	0.3	46
R6	1	74.2	4.0	11.6**	106
	2	89.6	-	4.5**	117
	3	97.2	-	2.6**	130
R7	1	75.9	2.1	17.0	117
	3	94.3	-	4.5	107

*Sample 1: at start of test
Sample 2: after dry CO_2 contact
Sample 3: at end of test

**Tin interferes with the analysis for sulfide. The true sulfide concentrations are probably higher

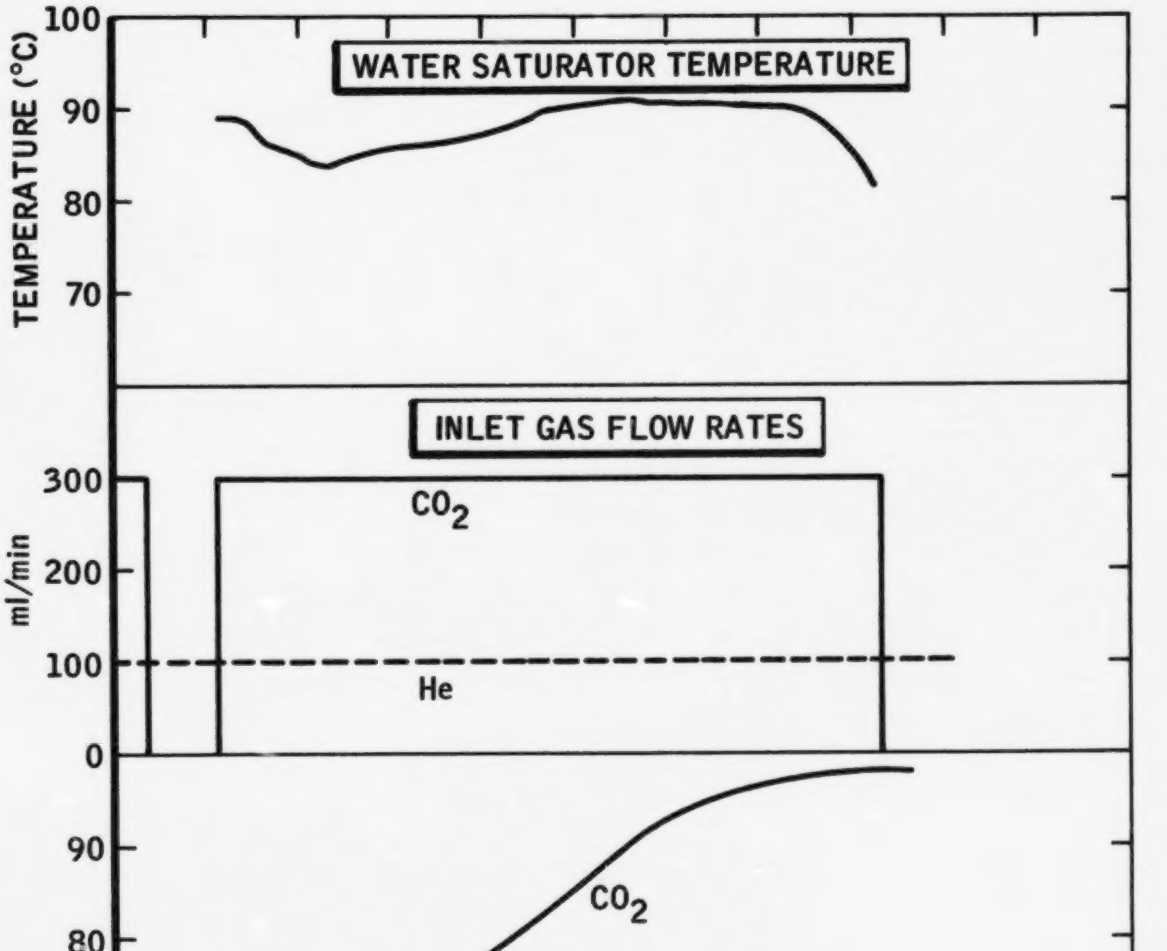
The exit gas streams were analyzed periodically, and the relative concentrations of carbon dioxide and hydrogen sulfide determined. These data are plotted in Figures 23-29, which also show the inlet carbon dioxide flow rates, the helium purge gas flow rates, and the water saturator temperatures as functions of time for each test.

Sulfur balances were made for each test. They are given in Table 31. The amount of sulfur initially present was calculated from the melt sulfide concentration and the melt height, measured with the sampling tube. A melt specific gravity of 2 (pure carbonate eutectic melt) was assumed for this. In tests R1 and R7, the melt heights and sulfide concentrations at the beginning of the tests (after the reduction step) were used to calculate the initial amount of sulfur. For the other tests, the compositions and melt heights at the end of step 1 (the dry carbon dioxide contact period) were used. The sulfur evolved as hydrogen sulfide was collected in an aqueous sodium hydroxide trap, and measured by a total sulfur analysis of the trap contents.

TABLE 31

SULFUR BALANCES

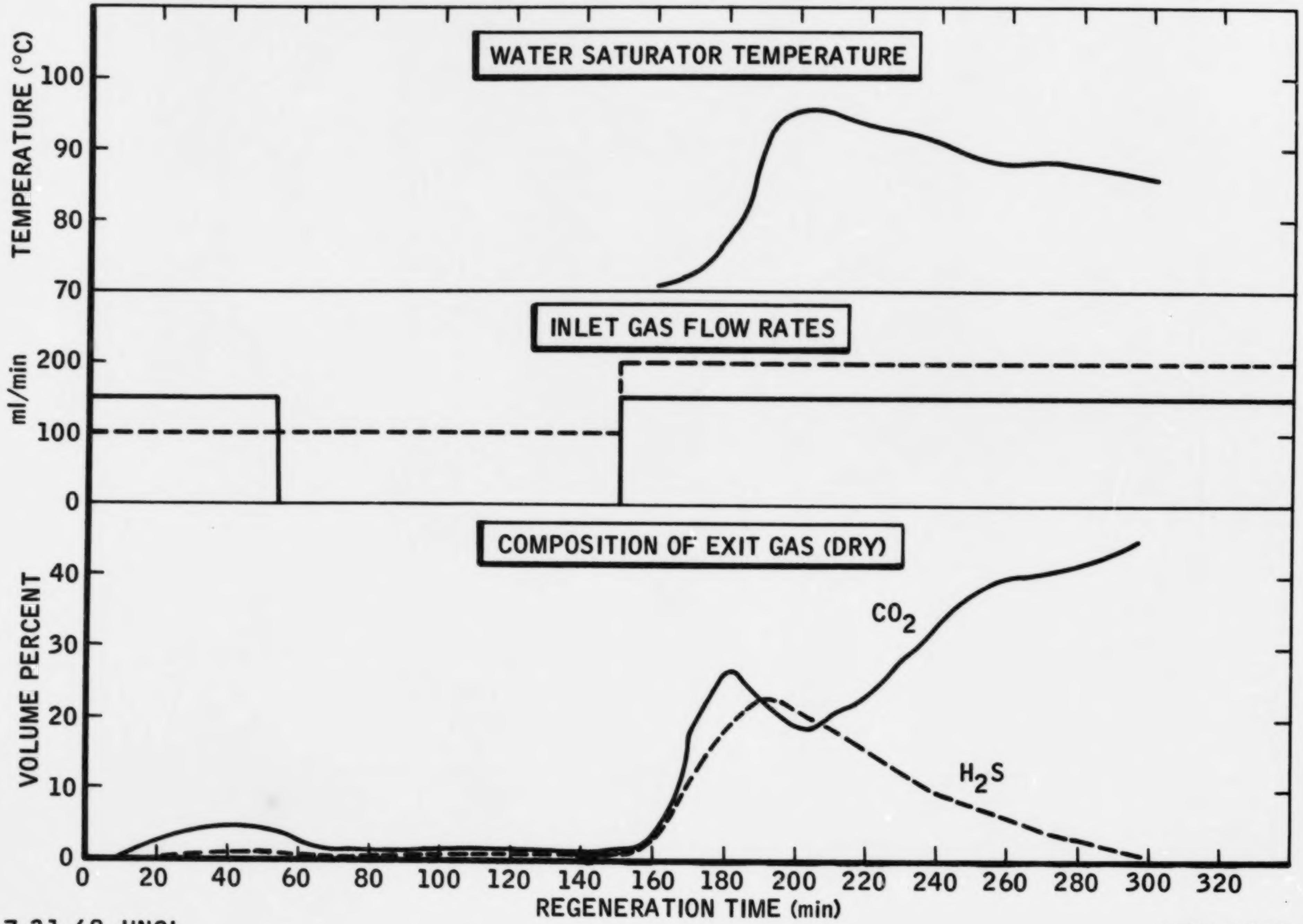
Test	Initial M_2S (g)	Recovered H_2S (as M_2S) (g)	Percent Recovered
R1	40.5	28.4	70
R2	26.5	25.0	94
R3	43.2	14.9	35
R4	32.9	23.2	70
R5	31.4	17.6	56
R6	27.3	1.1	4
R7	48.2	19.1	40



7-31-68 UNCL

7732-4022

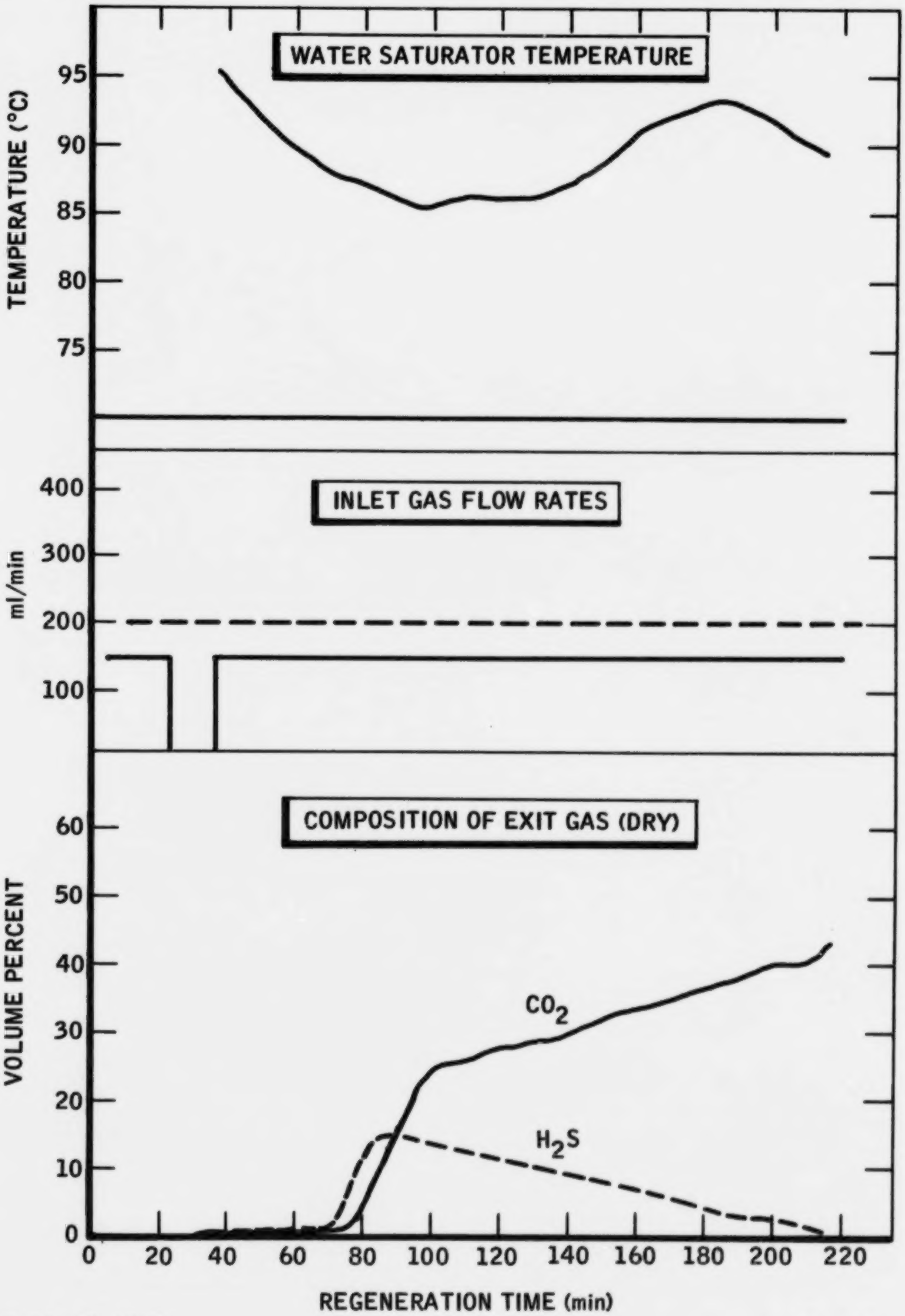
Figure 23. Regeneration of Melt R1



7-31-68 UNCL

7732-4021

Figure 24. Regeneration of Melt R2



7-31-68 UNCL

7732-4024

Figure 25. Regeneration of Melt R3

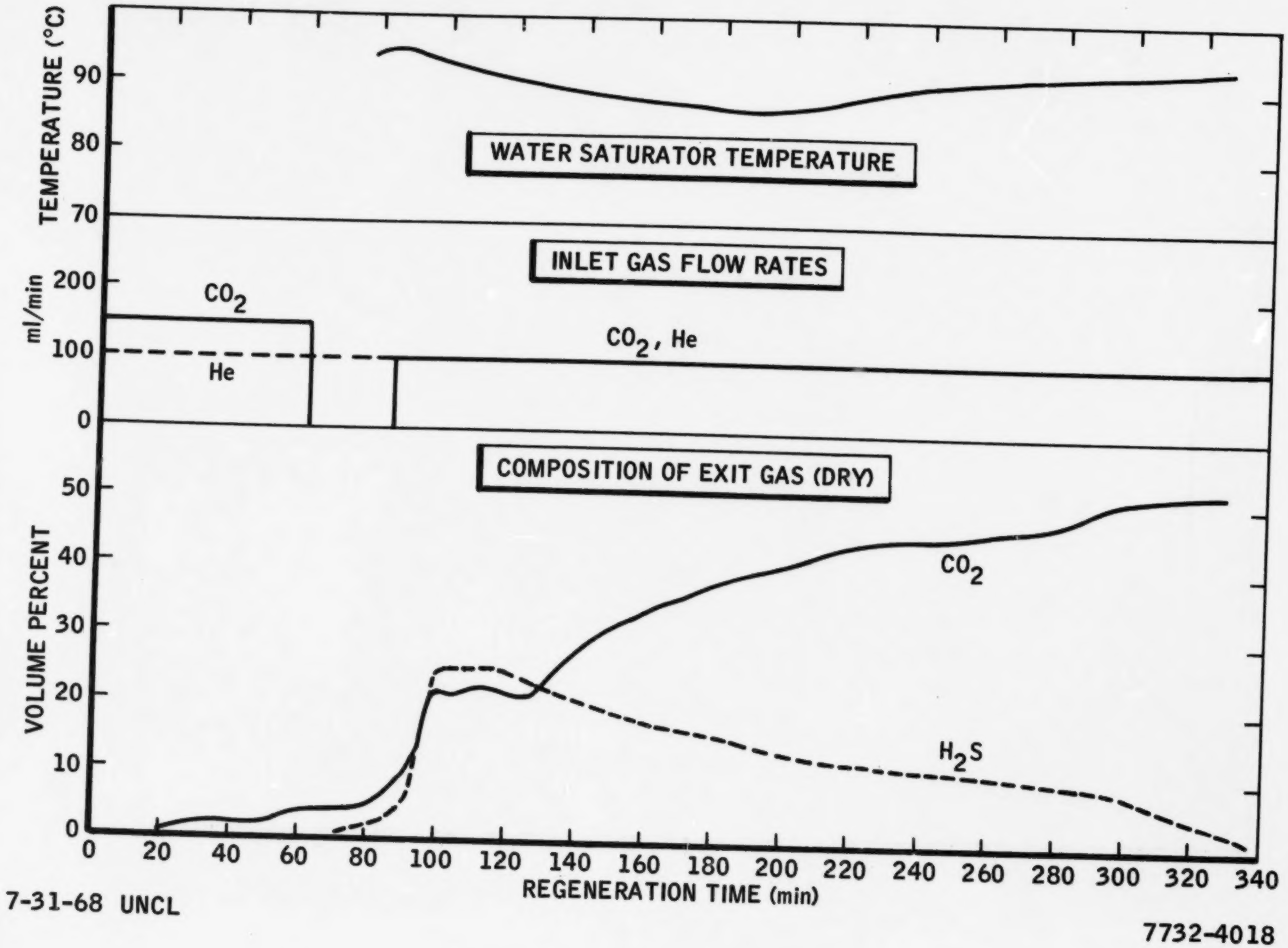


Figure 26. Regeneration of Melt R4

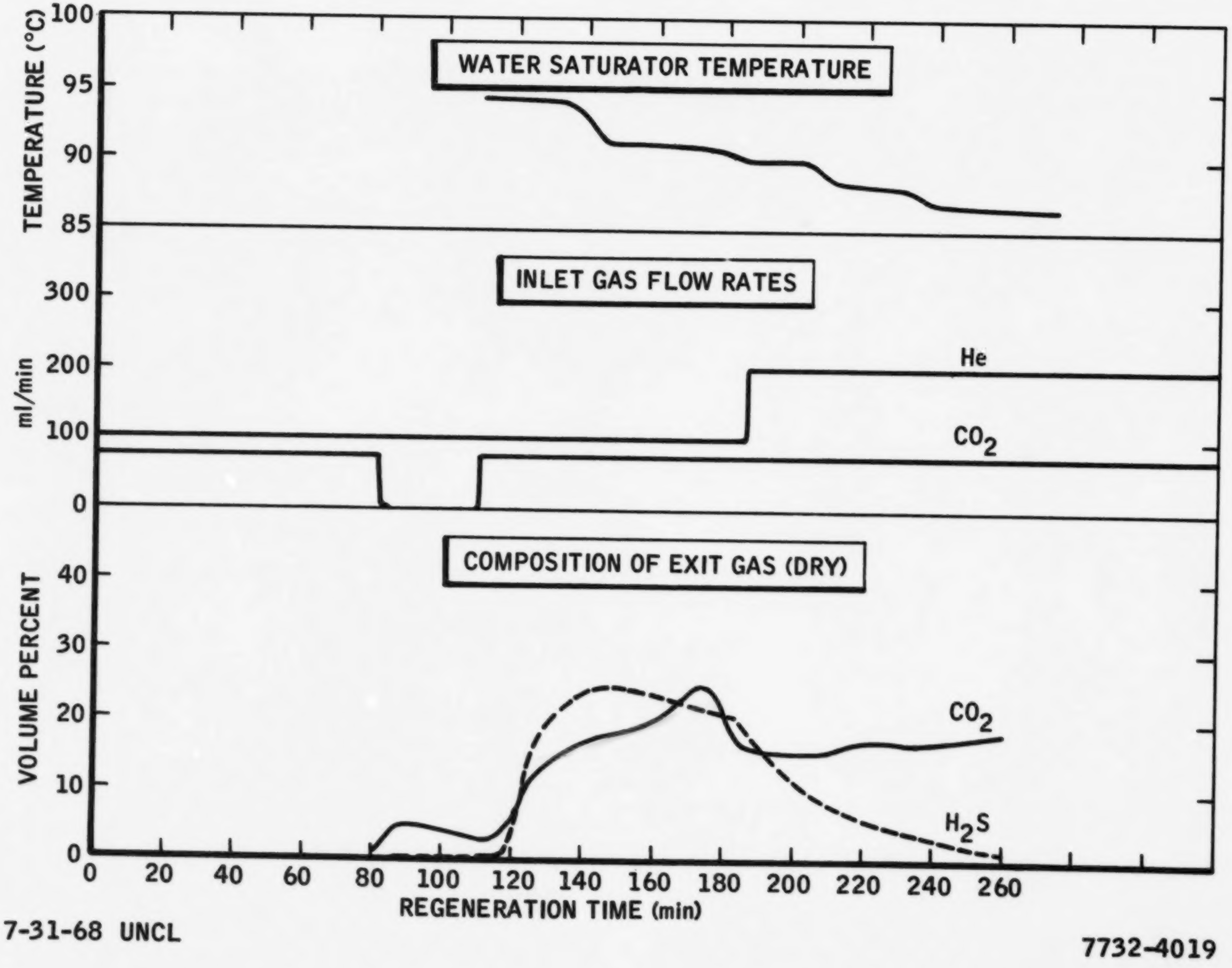
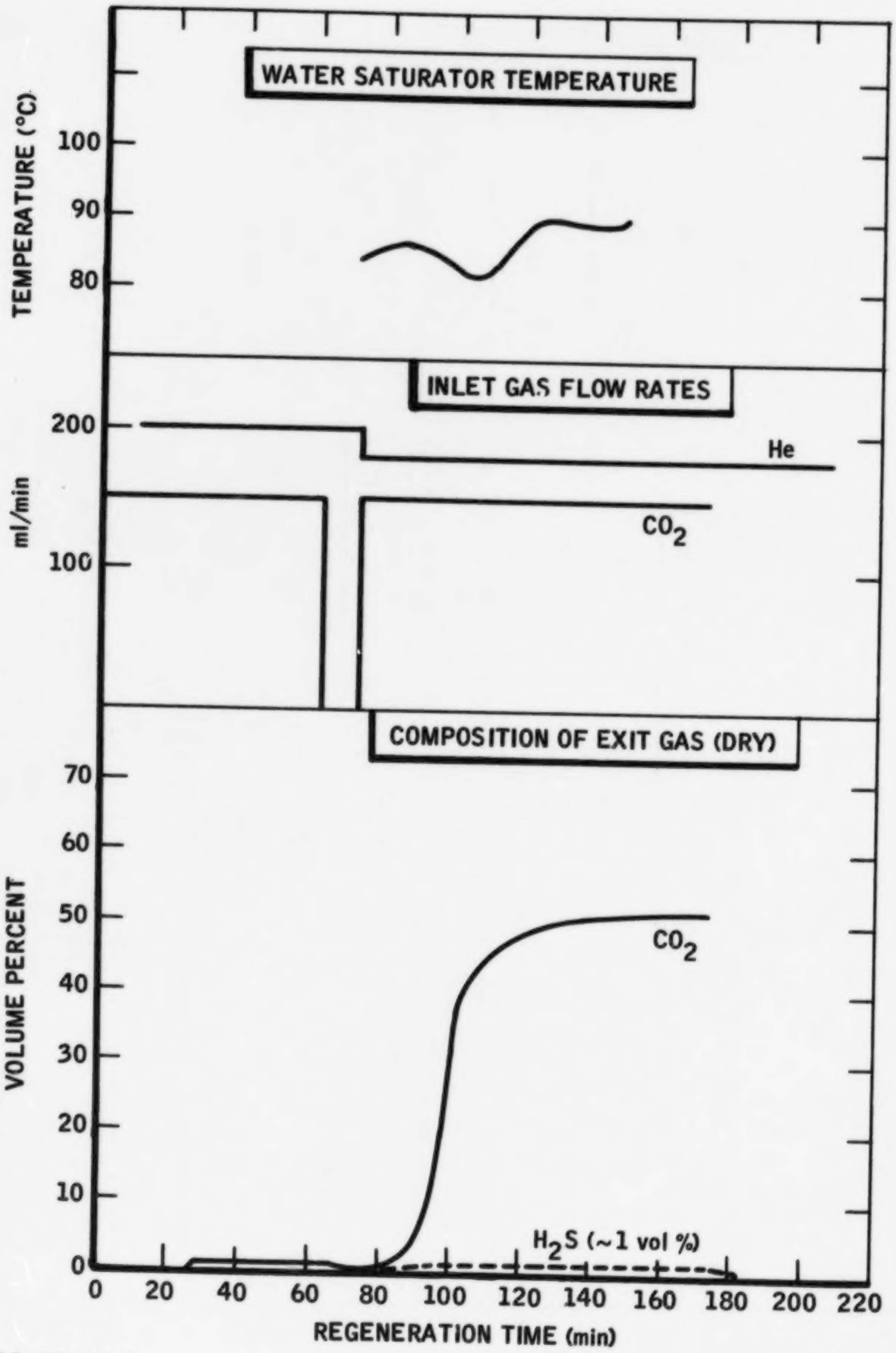


Figure 27. Regeneration of Melt R5



7-31-68 UNCL

7732-4023

Figure 28. Regeneration of Melt R6

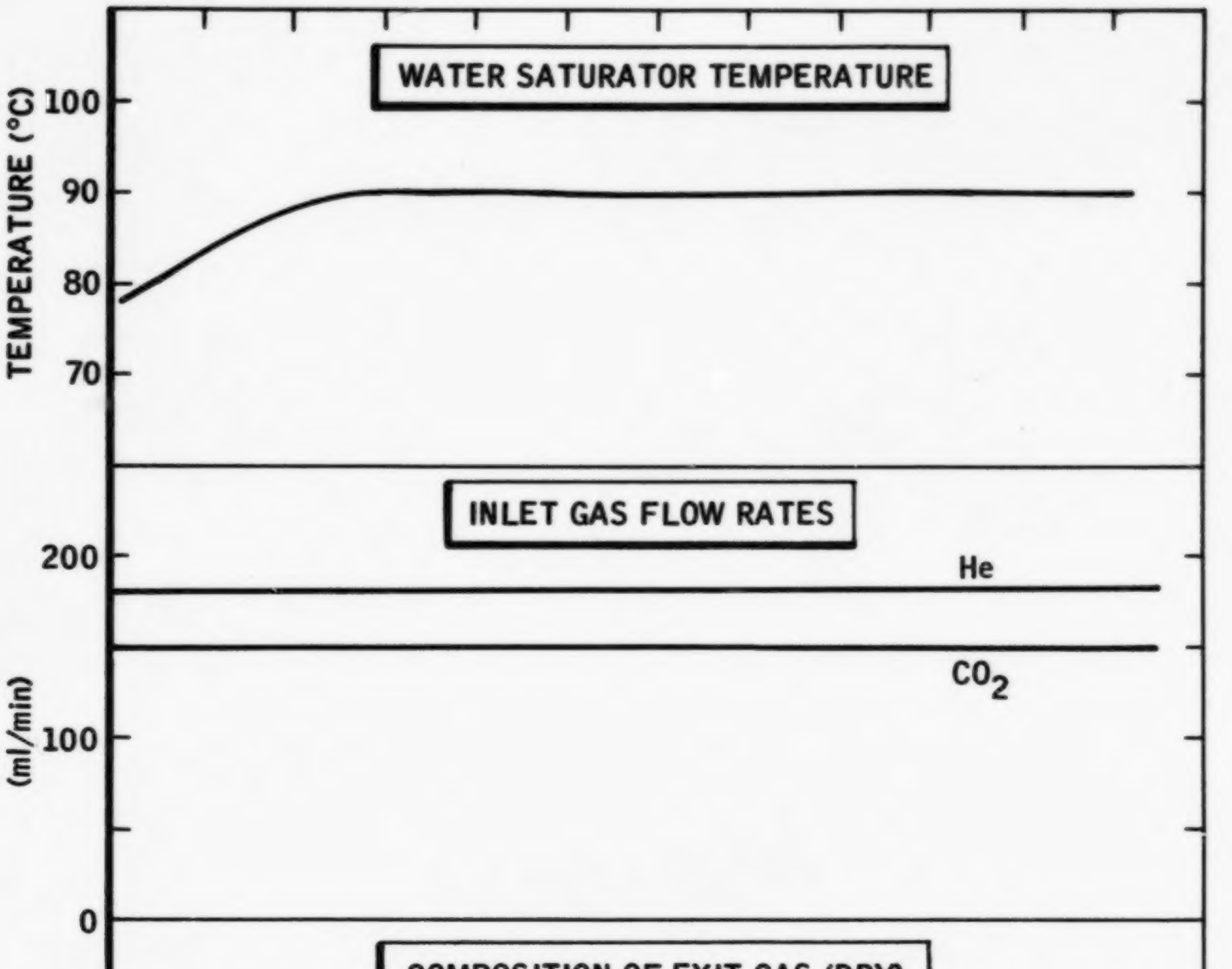


Figure 29. Regeneration of Melt R7

There was a 94% recovery of sulfur from test R2, while only 70% was recovered from test R1. The difference was probably due to the difference in gas flow rates. In test R1, the carbon dioxide and helium flow rates totaled 400 ml/min, and this high flow rate probably splashed some melt out of the crucible or up on the crucible walls, where it was not regenerated. This is supported by the data of Table 30, which shows that the melt volume decreased during the test. In contrast, the melt volume in test R2 actually increased during step 1, in which carbon dioxide was absorbed. The flow rate during step 1 of test R2 was only half that in R1, or 200 ml/min.

These results indicate that good sulfur recovery efficiencies can be achieved from uncatalyzed reduced melts. The optimum regeneration rate, however, will have to be determined with contactors wherein high gas throughputs can be used.

The melts used in tests R3, R4, R5, and R7 contained iron catalyst. Examination of Table 31 shows that this apparently had an adverse effect on the sulfur recovery efficiency, which ranged from 35% to 70%. This was due to a foaming or frothing which occurred when the gases were bubbled through the melt, even at low flow rates. The melt volumes all decreased significantly as a result of the treatment with the water vapor - carbon dioxide mixtures and consequent evolution of hydrogen sulfide. Examination of the melt containers after the tests showed that the missing material had formed a ring of iron- and sulfide-rich solid above the carbonate melt level. This material must be solid at the regeneration temperature, because it did not run back down into the melt. Also, further testing showed that this material does not give off hydrogen sulfide when treated with steam and carbon dioxide at temperatures between 840 and 1110°F (450 and 600°C).

Evidently the iron is combined with the sulfur as a sulfide or polysulfide, which is removed from the melt as a foam or froth and deposited on the crucible walls.

This raises two important questions; (1) can the sulfur recovery efficiency be improved, and (2) will the foaming interfere with the regeneration rate. It is not known whether or not the foaming will occur in countercurrent-type contactors, where the liquid can be kept in thin layers. If it does, then it may be necessary to remove the iron from the melt before regeneration, perhaps by filtration. The iron could then be returned to the reducer to be reused as a catalyst. If this is done, then the iron would not tie up the sulfur in the regenerator and recovery should be high.

If contactors can be found in which the foaming does not occur, then the iron will probably have to be removed from the melt after regeneration and returned to the reducer. Otherwise it would be removed in the fly ash filter, and fresh catalyst make-up would have to be provided with the reducer feed. A test has shown that iron deposit material can be separated from a molten carbonate suspension by filtration. Tests to filter the iron out of newly reduced melts will be tried soon.

The results of test R6 indicate that the tin catalyst interferes with regeneration much more than the iron did. Evidently tin sulfides or polysulfides are formed, which cannot be regenerated. Since tin does not appear to be as good a reduction catalyst as iron, this effect will not be studied further.

The melts remaining after the regeneration tests were all quite low in sulfide content except for that from test R7, there the remain- sulfide was probably combined with the iron. Thus, there does not appear to be a problem with reforming the carbonate for recirculation to the absorber.

Future tests will concentrate on studying effects of reduction catalysts on regeneration, and on determining regeneration rates in large surface area contactors.

5. Cycle Tests

The regeneration tests had shown that sulfide-containing melts could be regenerated to carbonate for recycle to the absorber. It was also necessary, however, to demonstrate that the same melt could be used over again in the process cycle, without loss of performance. This was done in an absorption-reduction-regeneration cycle test.

Three cycle tests were attempted. In the first two tests, steel bubbler-type contactors were used. In both cases, the absorption and reduction steps were successful but the melt foamed when rapid regeneration was attempted, plugging the gas exit lines. This foaming was similar to that observed in regenerating other melts containing iron in bubbler contactors. However, it may not be a problem when the regeneration is done in a countercurrent contactor, where the liquid phase will be kept in thin layers.

In these first two tests, the absorption steps were carried out by bubbling pure sulfur dioxide into the melt at a rate of 165 ml/min. Quantitative absorption occurred, with no sulfur dioxide detectable in the carbon dioxide stream given off. The reduction steps were then done with hydrogen at 1110°F (600°C). In both cases, 5 hours were required to achieve complete reduction. This was relatively rapid, considering the fact that a bubbler contactor with little surface area was used, and must reflect the catalytic activity of iron corrosion products. The first test regeneration was then tried with a water-saturated carbon dioxide flow rate of 2.5 ℓ/min, and resulted in extensive foaming which plugged the exit gas line. The second regeneration was attempted at a slower flow rate (0.9 ℓ/min) with the same result.

A third cycle test was then performed, using a graphite bubbler and slow regeneration rate, to study the effect of cycling on the carbonate melt. Two and two-thirds cycles were completed, with the results summarized in Table 32.

The three absorption steps were all quantitative, with no sulfur dioxide detectable in the off-gas. It should be noted that the second and third absorptions were done with melts containing 19% and 10% sulfate, respectively, with no detectable loss in capacity for sulfur dioxide, or in absorption rate. This is significant, because it shows that the process can be operated successfully with incompletely-reduced melts.

The first regeneration step was quite successful, and yielded essentially pure carbonate. The time required (180 min) was probably determined by the low reactant feed rate (150-300 ml/min of water-saturated carbon dioxide) rather than by the rate of reaction. Sulfur recovery was also good, 90% being recovered as hydrogen sulfide and the remainder probably also evolved but lost during sampling.

The first reduction step was very slow, due to the combination of (1) no iron catalyst present, (2) low surface area available, and (3) relatively low temperature (1050°F). The reduction was so slow that it was terminated after ~ 11½ hours, although only 36% of the sulfate and sulfite was reduced. The incompletely-reduced melt was then completely regenerated to carbonate plus sulfate, with only 0.2 wt % sulfide remaining. This time, however, only 70% of the sulfur was recovered as hydrogen sulfide. It is thought that

TABLE 32

RESULTS OF CYCLE TEST IN GRAPHITE SYSTEM

Step	Time (min)	Temp (°F)	Gas and Flow Rate (ml/min)	Melt Composition (wt %)				Comments
				M_2CO_3	M_2SO_3	M_2SO_4	M_2S	
Start	0	905	He, 200	91.0	0	-	11.1	Melt as prepared
Regeneration	180	905	CO_2+H_2O, 150-300	99.4	0	-	0.2	90% H_2S recovery
Absorption	60	905	SO_2, 165	64.5	27.2	3.7	0.2	Complete absorption
Reduction	247	1050	H_2, 1100	68.2	0	21.2	10.2	29% reduced
	683	1050	H_2, 1100	67.5	0	19.3	11.7	36% reduced
Regeneration	208	860	CO_2+H_2O, 150	81	0	19.1	0.2	70% H_2S recovery
Absorption	50	896	SO_2, 165	58.5	17.2	21.1	0.4	Complete absorption
Reduction	185	1290	H_2, 1100	61.9	0	8.1	28.6	Note 1
Regeneration	217	880	CO_2+H_2O, 150	84.9	0	9.6	0.3	90% H_2S recovery
Absorption	40	880	SO_2, 165	45.7	7.5	39.8	3.4	Complete absorption

Note 1. An excess of sulfide (~ 10 wt %) was found at the end of this reduction step. It may have come from sulfide-rich foam formed during the previous regeneration step, which solidified above the melt until the temperature was raised for the reduction step. This would also account for the low sulfur recovery of the previous regeneration step.

this relatively low recovery was due, in part at least, to a sulfide-rich foam freezing out above the melt and not being regenerated. Further evidence for this was obtained at the end of the second reduction step, when about 10 wt % extra sulfide was found in the melt. This could have been due to the foam melting at the higher reduction temperature, and recombining with the rest of the melt.

The second reduction was done at 1290°F, at which temperature ~ 60% of the sulfate was reduced in 3 hours.

The third regeneration was also essentially complete, with good sulfur recovery.

This cycle test demonstrated, as expected, that regenerated carbonate does not lose its capacity for absorbing sulfur dioxide, even when a large amount of sulfate is recirculated. However, it was not an exact demonstration of the reference process cycle, in which the reduction and regeneration will be done in two different large-surface-area contactors, instead of a single bubbler contactor. Also, a catalyst will probably be required in the reduction step. Future studies should yield the optimum reduction conditions. After this, cycle tests will be repeated with different contactors, to study the regeneration rate, the effect of reducing catalyst on regeneration, and other potential process problems.

6. Regeneration Equilibrium Studies

There is very little thermodynamic data available for lithium and potassium carbonate and sulfide. This makes it impossible to perform a thermodynamic analysis of the reactions involved in regenerating a melt of the mixed carbonates. However, there is sufficient data that the regeneration of sodium carbonate can be studied. The reaction involved is

$$Na_2S(\ell) + H_2O(g) + CO_2(g) \rightleftharpoons Na_2CO_3(\ell) + H_2S(g) \qquad (21)$$

The standard free energies of formation of the reactants and products are available for this reaction in reference 5. From these data, the standard free energy changes of the reaction and the reaction equilibrium constants can be calculated. These values are listed in Table 33.

TABLE 33

FREE ENERGY AND EQUILIBRIUM CONSTANTS
FOR THE SODIUM REGENERATION
REACTION (Reaction 21)

Temperature		ΔF° (kcal/g mole)	K
(°C)	(°F)		
427	800	-5.95	71.94
527	980	-3.16	7.30
627	1160	-0.53	1.34
727	1340	+1.96	0.37
827	1520	+4.33	0.14
927	1700	+6.60	0.065

These data indicate that the equilibrium favors the regeneration reaction at lower temperatures (below about 1200°F) and that the reverse reaction, i.e. the absorption of hydrogen sulfide by carbonate, is favored at higher temperatures. To investigate this experimentally, two tests were performed to measure the ability of the mixed carbonate melt to absorb hydrogen sulfide from mixtures of hydrogen sulfide and carbon dioxide. The test conditions are listed in Table 34.

To follow the progress of the test, the exit gas stream was analyzed by gas chromatography, after removing the evolved water with magnesium perchlorate. The gas analyses were used to calculate the fraction of

TABLE 34

HYDROGEN SULFIDE ABSORPTION TEST CONDITIONS

	First Test	Second Test
Temperature	930°F (500°C)	1150°F (620°C)
Pressure	1 atm	
CO_2 Flow Rate	370 ml/min	
H_2S Flow Rate	130 ml/min	

the hydrogen sulfide which was absorbed by the melt. Melt samples were also taken at the start, middle, and end of each test and analyzed. The results are listed in Table 35.

TABLE 35

HYDROGEN SULFIDE ABSORPTION TEST RESULTS

Temperature (°F)	Time (min)	Percent H_2S Absorbed	Melt Composition (wt %)	
			M_2CO_3	M_2S
930	0	100	100	0
	30	60	95.3	4.7
	53	49	94.4	5.6
1150	0	100	100	0
	30	82	93.8	6.2
	57	52	89.0	11.0

The results show that the melt absorbs hydrogen sulfide at both temperatures, and that more is absorbed at 1150°F than at 930°F.

The data of Table 35 can also be used to calculate the equilibrium constants for the mixed melt regeneration reaction. These values are shown compared to the theoretical values for the sodium regeneration reaction in Table 36.

TABLE 36

COMPARISON OF EQUILIBRIUM CONSTANTS

Temperature (°F)	Temp (min)	Equilibrium Constant (K)	
		Experimental, for Li, Na, K melt	Theoretical, for Na melt*
930	30	13	12.5
	55	16	12.5
1150	30	3.1	1.5
	57	6.7	1.5

*By graphical interpolation of the data of Table 33

The comparison is quite good at 930°F, and poor at 1150 F. The differences between the experimental and theoretical values must be due to one or more of the following reasons:

a. Error in the experimental data, suggested further by the differences in the experimental K values at different melt sulfide concentrations

b. The differences between mixed-melt and pure sodium equilibria

c. Errors in the thermodynamic data

d. Failure to achieve equilibrium

e. A regeneration reaction mechanism more complicated than that of equations 10 and 21.

It is impossible to conclude that equilibrium was or was not achieved during the tests, because there are not enough data and the data are not sufficiently accurate. Future regeneration tests will yield more data, which should make it possible to determine whether equilibrium is achieved or not, and which should also provide information about the regeneration reaction mechanism.

The carbonate melt appears to be a useful absorption material for separating hydrogen sulfide from gas mixtures containing carbon dioxide, e.g., sour natural gas. Dilute gases could be stripped of their hydrogen sulfide by absorption in carbonate, and then the sulfide regenerated to yield a concentrated gas. The use of the carbonate melt to absorb hydrogen sulfide from gas streams containing carbon dioxide appears to be a significant and novel discovery.

B. CORROSION STUDIES

Before the Molten Carbonate Process can be practical, it is necessary to find materials of construction which can withstand corrosion under the process conditions. Corrosion due to the process melts was of first concern, since little was known about it. At different places in the process there are melts of pure carbonate, carbonate plus sulfite and sulfate, and carbonate plus sulfide, and all of these must be contained in vessels and circulated through pipes. Initial efforts were therefore directed toward finding structural materials which would withstand corrosion by these different mixtures of molten salts.

1. The Test Program

A screening procedure was used to eliminate from further testing those materials which corroded rapidly. This consisted of 50-hour tests at 930°F in pure carbonate melts and in melts of carbonate and sulfide. Materials which exhibited low corrosion rates during these tests were then candidates for long-term tests, to verify their corrosion resistance. The long-term tests were done in rotating capsules, to simulate the process flow conditions somewhat. The procedures used in both the screening tests and long-term tests are described in more detail below.

Corrosion studies done by Janz, et al.(5) had shown that type 347 stainless steel resisted corrosion by pure carbonate melts quite well. Because of this, long-term tests of this material were started immediately, without waiting for the results of a screening test. Then, after the long-term tests were started, screening tests of many different materials were begun.

2. Screening Tests

In these tests, two to four test specimens of each material were suspended in static pools of melt for 50 hours, and then removed and examined. Melts of pure carbonate eutectic and of carbonate eutectic plus 20 wt % sulfide were used. Sulfite- and sulfate-containing melts were not used for these screening tests, because they were found to be less corrosive for type 347 stainless steel than the sulfide melts.

The test specimens were usually thin rectangular strips, about 4 in. by 1/4 in. and 0.03 in. thick. Each specimen was carefully cleaned, weighed, and measured before the test, and then re-weighed and remeasured after the test. In this way the change in weight and in thickness due to corrosion could be determined. Also, after each test, the specimens were examined microscopically for intergranular corrosion in areas which had been submerged in the melt, at the melt interface, and above the melt interface.

The preliminary screening tests were done at 930°F; later, promising materials were also tested at 1110°F and 1290°F.

a. Tests at 930°F (500°C)

The materials which have been given screening tests at 930°F are listed in Table 37. The compositions of the alloys in this table are all listed in Appendix C.

A large fraction of these materials were eliminated by the screening tests, either because they exhibited a large weight loss or had deep intergranular corrosion. The sulfide melt was by far the more corrosive of the two in all cases, and could have been used alone to determine maximum corrosion. However, the carbonate corrosion tests were also important, since some

TABLE 37

MATERIALS GIVEN CORROSION SCREENING TESTS AT 930°F

Stainless Steels

300 Series: Types 304, 304L, 310, 316, 321, 347
400 Series: Types 405, 410, 430, 446

Other Iron-Based Alloys

Armco V iron, type 1020 steel, Carpenter 20 Cb3, Multimet

Nickel-Based Alloys

Nickel 200, Nickel 201
Inconel 600 and 702
Hastelloy B, C, G, N, and X
Monel 400 and K500
Tophet A (80% Ni, 20% Cr)

Cobalt-Based Alloys

Haynes 25

Other Metals

Gold and palladium-20% gold alloy
Niobium
Tantalum
Titanium
Vanadium
Zirconium and Zircalloy II

Non-Metals

Graphite
Silica
Zirconia
Magnesia
Alumina

large components, e.g. the scrubbers, will probably not be exposed to melts containing sulfide. A low-cost material which resists corrosion in the carbonate melt but not in the carbonate-sulfide melt thus should still be tested further.

Those materials which were found to warrant further testing are listed in Table 38.

TABLE 38

MATERIALS WARRANTING FURTHER TESTING

Stainless Steels:	Types 304L, 310, 347
Iron-Based Alloys:	Armco V iron, type 1020 steel, Multimet
Nickel-Based Alloys:	Hastelloy G, N, and X
Cobalt-Based Alloy:	Haynes 25
Other Metals:	Tantalum, titanium
Non-Metals:	Graphite, zirconia, magnesia, alumina

The results of the screening tests for these materials are listed in Table 39, where the corrosion rates calculated from weight loss, the decrease in test specimen thickness, and the type and depth of corrosion determined from microscopic examination are given.

Type 304L is a relatively inexpensive low-carbon stainless steel. It exhibited very little corrosion in carbonate, and moderate corrosion in carbonate-sulfide, with no intergranular penetration by either melt. Its corrosion resistance was better than that of type 304, 316, or 321, and hence it was chosen over them for further testing. Type 310 stainless is a high temperature alloy; its behavior was similar to that of type 304L.

TABLE 39

CORROSION OF METALS IN MOLTEN SALTS

(50 Hours Exposure at 930°F)

Material	Melt Composition (mole %)		Corrosion Rates (mg/cm^2/hr)					Decrease in Thickness (mils)	Type of Corrosion and Depth of Penetration[a] (mils)		
	M_2CO_3	M_2S	1	2	3	4	Ave.		Melt	Interface	Gas
304L	80	20	-	-	0.254	0.243	0.249	0	S-1/8	S,F-2	S,F-2
304L	100	-	-	-	-0.0010	-0.0011	(-0.0011)	0	S-1/2	S-1	S-1
310	80	20	0.166	0.196	0.236	0.200	0.200	1	S,I-1/4	S-1/4	S-1/4
310	100	-	0.0007	0.0004	0.0013	0.0011	0.0009	0	S-1/2	S,I-1/2	I-1/2
347	80	20	0.622	0.652	0.662	0.696	0.658	1	S-0	T,I-1/4	I,S-1/2
347	100	-	0.0146	0.0138	0.0148	0.0146	0.0145	0	S-0	I-1/4	I-1/4
347	80 (20% M_2SO_3)	-	0.123	0.123	0.137	0.132	0.128	0	S-0	S-0	S-0
Armco V	80	20	-	-	0.643	0.662	0.653	0	I-1/2	S,I-1	S,I-1
Armco V	100	-	-	-	0.0101	0.0091	0.0096	0	I-1/8	I-1/8	I-1/2
1020	80	20	-	-	0.620	0.629	0.625	0	S,I-1	S,I-1	S,I-1
1020	100	-	-	-	0.0110	0.0108	0.0109	0	S-1/8	S-1/8	S-1/8
Multimet	80	20	-	0.0218	0.0163	0.0198	0.0193	0	S-1/4	S-1/2	S-1/2
Multimet	100	-	-	0.0008	0.0010	0.0004	0.0007	0	S-1/8	S-1/4	S-1/2
Hastelloy G	80	20	-	-	0.0168	0.0144	0.0157	0	S-1/8	S-0	S-0
Hastelloy G	100	-	-	-	-0.0007	-0.0004	-0.0006	0	F-1/8	F-1	I,S-1/8
Hastelloy N	80	20	-	-	0.0784	0.0736	0.0760	1/2	I-0	I-0	I-1
Hastelloy N	100	-	-	-	0.0006	0.0007	0.0007	0	I-1/4	F-1/8	I-1/8
Hastelloy X	80	20	-	-	0.0636	0.0956	0.0796	0	S-0	S-0	S-0
Hastelloy X	100	-	-	-	-0.0012	-0.0012	(-0.0012)	0	S-0	S-0	S-0
Haynes 25	80	20	-	-	0.0032	0.0031	0.0032	0	S-0	S-0	S-0
Haynes 25	100 -	-	-	-	0.0008	0.0014	0.0011	0	S-0	S-0	S-0
Tantalum	80	20	-0.0074	-0.120	-0.148	-0.0110	(-0.001)	0	I-1/8	I-1/8	I-1/8
Tantalum	100	-	-0.0076	-0.0113	-0.0080	-0.114	(-0.096)	0	I-1/8	I-1/8	I-1/8
Titanium	80	20	-	-	0	0	0	0	S-0	S-0	S-0
Titanium	100	-	-	-	-0.0001	-0.0001	-0.0001	0	S-0	S-0	S-0
Graphite[b]	80	20	-	-	-	0.002	0.002	0	P-1/2	P-1/2	P-1/2
Graphite[b]	100	-	-	-	-	0.003	0.003	0	S-1/8	S-1/8	S-1/8
Graphite[c]	80	20	-	-	-	0.003	0.003	0	S-1/8	S-1/8	S-1/8
Graphite[c]	100	-	-	-	-	0.002	0.002	0	P-1/4	P-1/4	P-1/4
Graphite[d]	80	20	-	-0.004[e]	-0.82[f]	-0.82[g]	(-0.37)	0	Not observed		
Graphite[d]	100	-	-	0.013[e]	0.006[f]	0.002[g]	0.007	0	Not observed		
ZrO_2	80	20	-	-	-0.5	-0.4	(-0.4)	0	Not observed		
ZrO_2	100	-	-	-	-0.4	-0.4	(-0.4)	0	Not observed		
MgO	80	20	-	-	-0.9	-0.8	(-0.9)	0	Not observed		
MgO	100	-	-	-	-0.8	-0.7	(-0.8)	0	Not observed		
Al_2O_3	80	20	-	-	0.0001	0.0000	0.0001	0	Not observed		
Al_2O_3	100	-	-	-	-0.0002	-0.0001	-0.0002	0	Not observed		

[a] I = intergranular attack, S = general surface attack, F = film, P = pits

[b] AGSX graphite #571 X

[c] Carborundum Metal Pumping Services graphite

[d] Graphite raschig ring 571B

[e] Sample exposed to vapor only

[f] Sample exposed to both melt and vapor

[g] Sample completely immersed in melt

The other stainless steel retained for further testing was type 347. This alloy was tested in a melt of carbonate plus 20 wt % sulfite, as well as in the carbonate and carbonate-sulfide melts. The sulfite-containing melt was more corrosive than pure carbonate but less corrosive than carbonate plus sulfide. The sulfide melt corrosion rate of type 347 was relatively high, but there was almost no intergranular corrosion in any of the three melts. This behavior was different from that of types 304, 316, and 321, which were rejected because significant intergranular corrosion was found. The difference is probably due to the type of carbon stabilizer used in the different alloys. Type 304 and 310 are unstabilized, type 316 has a molybdenum stabilizer, type 321 is titanium-stabilized and type 347 has a niobium stabilizer. Evidently niobium is the best stabilizer. Type 304L is a special low-carbon alloy, which fact probably accounts for its resistance to intergranular corrosion.

Armco V iron and type 1020 steel are both relatively inexpensive, and they both exhibited about the same corrosion resistance as type 347 stainless but with somewhat more intergranular penetration. The cost factor aids in their selection for further testing.

The other alloys (Multimet, the Hastelloys, and Haynes 25) are more expensive than stainless steel, but they had very low corrosion rates in the sulfide melts, and were chosen for further testing for this reason.

The elemental metals titanium and tantalum were also quite corrosion resistant. They will be tested further if the less expensive materials do not prove suitable after long-term tests.

Graphite and alumina were quite corrosion resistant, and exhibited very low weight losses. Zirconia and magnesia also resisted corrosion well, but appeared to be slightly permeable to the melts; the specimens all gained weight. One graphite specimen also gained weight in the sulfide melt, perhaps due to absorption of melt. The graphite, zirconia, magnesia, and alumina all withstood corrosion well enough to warrant further testing.

b. Tests at 1110°F (600°C)

These tests were carried out primarily to find candidate materials for use in the reduction reactor, where sulfide-containing melts must be handled and where temperatures of 1100°F or higher may be encountered. Only alloys which had shown at least fair corrosion resistance to sulfide melts at 930°F were tested at this higher temperature. The alloys tested are listed in Table 40.

TABLE 40

MATERIALS GIVEN CORROSION SCREENING TESTS AT 1110°F

Type 304L, 310, and 347 stainless steel
Multimet
Inconel 600 and 702
Hastelloy C, G, N, and X
Haynes 25

As expected, corrosion was generally much more rapid at 1110°F than at 930°F. Also, as in the 930°F tests, the melts containing sulfide were much more corrosive than the pure carbonate melts. All of the alloys of Table 40 resisted corrosion in pure carbonate quite well at 1110°F, but only four were sufficiently corrosion resistant in the carbonate-sulfide melts to justify further testing. These four are Multimet, Hastelloy G, Hastelloy X, and Haynes 25. The results of their corrosion tests are tabulated in Table 41.

TABLE 41

CORROSION OF METALS IN MOLTEN SALTS AT 1110°F

(50 Hours Exposure)

Material	Melt Composition (mole %)		Corrosion Rates ($mg/cm^2/hr$)			Decrease in Thickness (mils)	Type of Corrosion and Depth of Penetration[a] (mils)		
	M_2CO_3	M_2S	1	2	Ave.		Melt	Interface	Gas
Multimet	80	20	-	0.072	0.072	0	S,F-½	F-¼	F-¼
Multimet	100	0	-	0.0049	0.0049	0	F,I-¼	F,I-¼	F,I-¼
Hastelloy G	80	20	0.0404	0.0388	0.0396	0	F-¼	F-¼	F-¼
Hastelloy G	100	-	-0.0150	-0.0100	(-0.0125)	(-½)	F-¼	F-¼	F-¼
Hastelloy X	80	20	0.0963	0.101	0.0982	0	F-½	S,F-1	S-¼
Hastelloy X	100	-	-0.0112	-0.0107	(-0.0110)	0	F-½	F-½	F-¼
Haynes 25	80	20	0.0179	0.0216	0.0198	0	F-½	F-½	F-½
Haynes 25	100	-	-0.0048	-0.0045	(-0.0047)	0	S-¼	S-1/8	S-¼

[a] I = intergranular attack, S = general surface attack, F = film

The Multimet specimens tested in the sulfide melts had black films below the vapor-melt interface and grey films above, while in the pure carbonate melts the films were grey throughout. The average weight loss was moderate (0.072 $mg/cm^2/hr$ in the sulfide melt) and no change in thickness was measurable. Photomicrographs suggested that slight intergranular corrosion had occurred in both the pure carbonate melt and the melt containing sulfide. Some surface corrosion also occurred, but it was not severe and the intergranular penetration was not very deep. The rather thin films formed on the specimens in contact with both melts appeared to be quite protective.

The Hastelloy G specimens exposed to the sulfide melts were covered with a dark grey film, nearly black below the vapor-melt interface. The film on the specimens tested in pure carbonate was light grey, and somewhat mottled. It presumably was the cause of the slight increase (~ 1/2 mil) detected in the specimen thickness. There was no detectable change in thickness of the sulfide test specimens, and their weight loss was moderate. Photomicrographs showed a thin (~ 1/4 mil) film on the surface, and some evidence of surface roughening below the film. However, there was no intergranular corrosion, and the surface roughening did not appear serious enough to eliminate this alloy from further testing.

The Hastelloy X specimens exposed to the sulfide melt were covered with a black film that was lighter at the interface, while those exposed to pure carbonate retained their original grey color. The average weight loss of the sulfide test specimens was somewhat higher than for Multimet, but still moderate, and there was no measurable thickness change. The microscopic examination showed some slight surface roughening under a film approximaterly 1/2 mil thick, with no intergranular corrosion.

The Haynes 25 specimens exposed to the sulfide melt had a stable black film on their surfaces, while those exposed to carbonate had a mottled grey-black color. The weight loss in the sulfide melt was lowest of the four alloys (~ 0.02 $mg/cm^2/hr$) and no decrease in thickness could be measured. Little evidence of corrosion damage was found in the photomicrographs, which showed a film approximately 1/2 mil thick, but no intergranular corrosion in the sulfide melt and only slight surface roughening in the pure carbonate melt.

The four alloys discussed above (Multimet, Hastelloy G, Hastelloy X, and Haynes 25) will be tested for longer periods of time at 1110°F in sulfide melts. It should be stated that even though these alloys are not entirely corrosion resistant, they may contain sulfide melts satisfactorily.

To illustrate this, the corrosion rate of Haynes 25 (8-10 mils/yr based on the 50 hr tests) will probably actually be only about 1-4 mils/yr, since short term corrosion tests generally yield rates that are much too high (for diffusion limited corrosion). Corrosion rates of this magnitude can be tolerated and should not cause severe problems in a process plant.

The other alloys of Table 40 were all quite severely corroded. The type 304L, 310, and 347 stainless steels suffered severe general attack by the sulfide melts. Hastelloy C and N and Inconel 600 and 702 were less severely attacked, but did not stand up as well as Hastelloy G and X and Haynes 25. Therefore, they will not be tested further.

The SS 310 specimens were polished on three sides and left as-received on the fourth side. This treatment apparently affected the mechanism of corrosion in the sulfide melt. After testing, the specimens were coated with a black film which was easily removed and not protective on the three sides that had been polished. The film that had been formed on the fourth side was more tenacious. Polishing may have introduced strains in the metal that did not permit tenacious films to form, leading to more rapid corrosion of the polished surfaces. This introduces another variable, surface preparation, which will have to be considered in future corrosion tests.

c. Tests at 1290°F (700°C)

These tests were carried out to find materials for severe service, such as in high temperature reduction reaction vessels. The four alloys which resisted corrosion best at 1110°F were tested, along with types 310 and 347 stainless steel and Carpenter 20 Cb3. The last three were included primarily to determine if a protective film would be formed on iron-based alloys at 1290°F.

The results of these tests are listed in Table 42.

TABLE 42

CORROSION OF METALS IN MOLTEN SALTS AT 1290°F
(50 Hours Exposure to Carbonate-20% Sulfide Melts)

Material	Corrosion Rates ($mg/cm^2/hr$)			Decrease in Thickness (mils)	Type of Corrosion and Depth of Penetration[a]		
	1	2	Avg.		Melt	Interface	Gas
Multimet	4.4	4.3	4.3	2	Incomplete		
Hastelloy G	0.94	0.86	0.90	3	Incomplete		
Hastelloy X	0.34	0.98	0.66	2	F-½	F-6	F-1
Haynes 25	0.58	0.88	0.73	3	F-1	F-5	F-1
SS 310	11.6	11.6	11.5	70	Incomplete		
SS 347		Destroyed		>17	F-16	F-8	I-4
Carpenter 20 Cb3	5.4	5.3	5.3	5	Incomplete		

[a] F = film, I = intergranular attack

The types 310 and 347 steels and Carpenter 20 Cb3 were severely attacked at the interface, while the Multimet and 347 disintegrated below the melt-gas interface.

Hastelloy G and Hastelloy X also were most severely attacked at the melt-gas interface, where thick hard films built up. From the photomicrographs of Hastelloy X, it appeared that corrosion proceeded by a surface mechanism, rather than by intergranular penetration. The surface appeared to be coated with several different types of films, perhaps indicating that a protective film could not form at this temperature.

The Haynes 25 specimens had less interfacial corrosion than the other alloys. The photomicrographs indicated that stress corrosion had occurred. Haynes 25 is a very hard alloy, and apparently some pre-treatment before the corrosion test introduced cracks or stress lines which were not annealed out. Below the melt level a mounting hole was punched in the specimen, and surrounding this mounting hole corrosion penetrated at various points up to about 1 mil. However, with proper annealing this type of corrosion probably would not have occurred. In general, the corrosion proceeded by a surface mechanism; there was no evidence of intergranular corrosion except for the stress corrosion.

None of the alloys tested resisted the sulfide melt corrosion well at 1290°F. However, pending the completion of the photomicrographic examinations, it appears that the further testing of Hastelloy G, Hastelloy X, and Haynes 25 is justified.

3. Long-Term Tests

These tests were performed to study the corrosion rates of materials not eliminated by the screening tests, and to verify their corrosion resistance. The tests were carried out by mounting corrosion test specimens inside type 347 stainless steel capsules, filling the capsules with the salt mixtures to be tested, sealing the capsules under a nitrogen atmosphere, and then rotating the capsules continuously at 15 or 23 rpm inside furnaces maintained at the test temperature. The capsules were inclined at 25°, so the lower portion of each of the four corrosion test specimens was always immersed in the melt while the upper portion of each specimen was in the melt about half of the time.

The first tests were done at 950°F to study type 347 stainless steel. Later tests of this alloy were also done at 1100°F and 1300°F, and other 1100°F tests are now in progress.

a. Tests of Type 347 Stainless Steel at 950°F

Five tests were performed at 950°F, with the mixtures and atmospheres listed in Table 43.

TABLE 43

TEST CONDITIONS, TYPE 347 LONG-TERM TEST AT 950°F

Capsule No.	Salt Mixture	Atmosphere
1	M_2CO_3 + 20 wt % M_2SO_3	N_2, 7 psig at 950°F
2	M_2CO_3 + 20 wt % M_2S	N_2, 7 psig at 950°F
3	M_2CO_3 + 20 wt % M_2SO_3	N_2 + 50 psig H_2O at 950°F
4	M_2CO_3	N_2, 7 psig at 950°F
5	M_2CO_3	N_2, 7 psig at 950°F

Capsule 5 was opened after 412 hours, and the test specimens examined. The results are listed in Table 44. The corrosion rate based on weight loss was found to be 0.0075 ± 0.0001 mg/cm^2/hr, or less than 3 mils of surface corrosion per year. This was only half the 0.0145 mg/cm^2/hr found in the carbonate screening test, indicating that the corrosion rate is probably high initially and then decreases.

No evidence of intergranular corrosion or pitting was found, but two types of films covered the surfaces of the test specimens and container where they were in contact with the melt. The outer film was much darker than the base metal and was probably the $LiFeO_2$ film reported by Janz(5)

TABLE 44

CORROSION OF TYPE 347 STAINLESS STEEL AT 950°F

Exposure (hr)	Melt Composition	Corrosion Rate (mg/cm^2/hr)					Decrease in Thickness (mils)	Type of Corrosions and Depth of Penetration[a] (mils)		
		1	2	3	4	Avg.		Melt	Interface	Gas
412	Carbonate	0.0074	0.0076	0.0077	0.0074	0.0075	0	S-0	S-0	S-0
1500	Carbonate + 20% Sulfide	0.0313	0.0309	0.0312	0.0309	0.0311	3	I-¼	I-½	I-½
1500	Carbonate + 20% Sulfite	0.0230	0.0205	0.0211	0.0197	0.0211	1	S-½	S-½	I-½
1500	Carbonate + 20% Sulfite[b]	0.0190	0.0180	0.0181	0.0189	0.0185	2	S-½	S-½	S-½

[a] S = general surface attack, I = intergranular attack

[b] Plus 50 psig H_2O at 950°F

when SS 347 was exposed to molten carbonate. This film varied in thickness from 0.2 to 0.5 mil where the sample was exposed to the melt, and was absent where no melt contacted the metal. The inner layer of film was indistinguishable from the base metal except that it did not etch properly. On the inside container walls not exposed to carbonate this layer was not present; after etching, the grains were outlined right up to the metal surface. The difference appears to be a result of contact with the molten carbonate, and may indicate a change in the composition of the intergranular material.

The tests with capsules 1, 2, and 3 were terminated after 1500 hours. The results are also tabulated in Table 44, and described below. The test with capsule 4 is continuing.

(1) Visual Examination. The specimens removed from all three melts did not appear to be damaged significantly, and there was no evidence of pitting. All specimens had a dark brownish-black coloration, and some specimens had a spotty appearance as if an outer film layer had flaked off during cleaning.

(2) Weight Loss. Based on weight lost, average corrosion rates of 0.0311, 0.0211, and 0.0185 mg/cm^2/hr were observed in the sulfide, sulfite and sulfite-H_2O melts, respectively. From these results and the results after 412 hours in carbonate, corrosion rates of 3, 9, and 14 mils per year can be predicted for 347 stainless steel in carbonate, carbonate-20% sulfite and carbonate-20% sulfide melts, respectively. It should be noted that the 1500-hour corrosion rate in the sulfide melt (0.0311 mg/cm^2/hr) was much less than the 0.658 mg/cm^2/hr found in the 50-hr screening test. This indicates again that the initial corrosion rate is much higher than the steady-state corrosion rate. Taking into account the fact that about half or more of the weight loss

observed in the dynamic tests had already occurred in the 50-hr static tests leads to predicted yearly corrosion rates of less than 1, 4 and 7 mils per year, respectively, in the three melts.

(3) Microscopic Examination. A protective film had formed on all specimens, particularly in the sulfite-containing melts. This film was about 1/4 mil thick and appeared to be slightly thicker on that portion of the specimen continuously exposed to the melt. A few breaks in this film were observed on the specimens exposed to sulfide, but these breaks did not seem to enhance local corrosion. Some intergranular corrosion was observed; the maximum depth of penetration was about 1/2 mil. The depth of penetration was constant and did not appear to depend upon the time during each revolution that the specimen was in contact with the melt.

On the basis of these results it appears that, at least at 950°F, stainless steel 347 will be quite satisfactory as a container material throughout the process.

The remaining test in pure carbonate (capsule 4) is continuing; it is planned to run this test for one year (8800 hours) and to terminate it in June, 1968.

b. Tests of Type 347 Stainless Steel at 1100°F and 1300°F

As the long-term 950°F tests were terminated, other tests of type 347 stainless steel at 1100°F and 1300°F were started. Melts of carbonate, carbonate plus 20 wt % sulfite, and carbonate plus 20 wt % sulfide were used at 1100°F, and pure carbonate only at 1300°F. These tests lasted for 1500 hours. The results are described below.

(1) Visual Observations. The specimens that were exposed to sulfide-containing melts completely disintegrated and were removed from the reaction vessel as small bits of metallic film. This material was black in

color and much thicker than the original metal specimens, indicating that the metal swelled as it corroded and probably broke into little pieces during the process. Thus, 347 stainless steel cannot be used as a container material for sulfide-containing melts at 1100°F.

The specimens exposed to sulfite at 1100°F were severely corroded; however, sufficiently intact specimens were recovered for mounting and microscopic examination. The edges and the corners of the specimens had completely dissolved, and the specimens were much thinner than they were originally. The metal was covered with a thick black film which was easily flaked off, indicating that it was not tenaciously held to the surface and therefore was not protective.

The specimens exposed to pure carbonate melt at 1100°F for 1500 hours were not severely attacked. They were coated with a black film that apparently was protective against further corrosion. The corners and the edges of these specimens were quite sharp, an indication that corrosion was not severe.

The specimens exposed to pure carbonate melt at 1300°F for 1500 hours were very severely corroded, and had disintegrated.

(2) Weight Loss. The weight of the specimens was determined before and after corrosion to determine the weight loss during the corrosion tests. Unfortunately, in all cases except where 347 stainless steel was exposed to pure carbonate at 1100°F, the specimens disintegrated to the point where good weight loss data could not be obtained. Those data obtained indicate that the corrosion rate at 1100°F in melts containing 20% sulfite was greater than 0.2 mg/cm^2/hr. In the test in sulfide-containing melts at 1100°F,

the corrosion rate was about 0.115 $mg/cm^2/hr$, and in pure carbonate at 1100°F, the corrosion rate was approximately 7×10^{-4} $mg/cm^2/hr$. However, 347 stainless steel completely disintegrates when it is exposed to pure carbonate at 1300°F, where the corrosion rate was greater than 0.2 $mg/cm^2/hr$. Thus, an increase in temperature of 200°F increased the corrosion rate over 300 times.

Long-term tests of Hastelloy G and Haynes 25 have been initiated at 1100°F. Melts of pure carbonate, carbonate plus 20% sulfide, and carbonate plus 20% sulfite are being used, and the tests will run for 1500 hours. They will be finished in April, 1968.

4. Future Work

Most of the screening tests have been completed; future work will center upon examining the more promising metals for longer periods of time and at higher temperatures. In general these tests will be for 1500 hours, and will involve both iron-based and nickel-based alloys. Hastelloy X, Multimet, Carpenter 20, 304L and 310 stainless steels, and 1020 steel will be tested for longer periods of time and/or at higher temperatures. A strong effort will be made to find a material that will not be corroded by melts containing sulfide, sulfite and sulfate at temperatures up to 1300°F. Zirconia, magnesia, alumina, and graphite will be tested at 1100°F. Water and CO_2 solubility in the various melts will be determined and the effect of their presence on corrosion of the more stable material will be studied. The effect of temperature cycling will be studied, and thermal loops will be operated to study the possible migration of alloy constituents.

C. CONTACTOR DEVELOPMENT

The purpose of this development effort is to design, build, test, and evaluate different types of gas-liquid contactors, both for scrubbing the flue gas and for regenerating the spent carbonate melts. Initial work concentrated on scrubber contactor development, because the process chemistry of the scrubbing step was most advanced. Work has since begun on reducer contactor development also.

1. Scrubber Contactor Development

a. The Test Stand

A test stand was constructed first, to provide for countercurrent melt and gas flow in carrying out the contactor tests. A schematic diagram of this test stand is shown in Figure 30. The required melt flow rate was so low (less than 10 lb/hr) that no suitable pump could be found to circulate the melt. Because of this, a once-through system was chosen, with the melt flowing from the reservoir through the test contactor to the receiver, without recirculation. Nitrogen gas pressure maintained above the melt in the reservoir forced the melt to flow, and the flow rate was controlled by a stainless-steel needle valve with a micrometer stem position indicator. This valve was calibrated, so that the desired flow rate could be obtained by setting the stem position correctly.

The first tests were done using pure mixtures of carbon dioxide and sulfur dioxide; later the effect of nitric oxide (NO) was also studied. In all cases, commercial cylinder gases were used. The gas flow rates were measured with rotometers, and the gas streams were then mixed, heated, and passed upward through the test contactor. After leaving the contactor, they were discharged into the laboratory fume vent system.

The contactor test stand was designed to provide gas flow rates as high as 250 scfh, and salt flow rates between 0.25 and 10 lb/hr. The gas flow rate capacity could provide a linear gas velocity of up to 30 ft/sec through a 1-in. diameter test contactor; this approximates the velocity which will be encountered in a commercial installation.

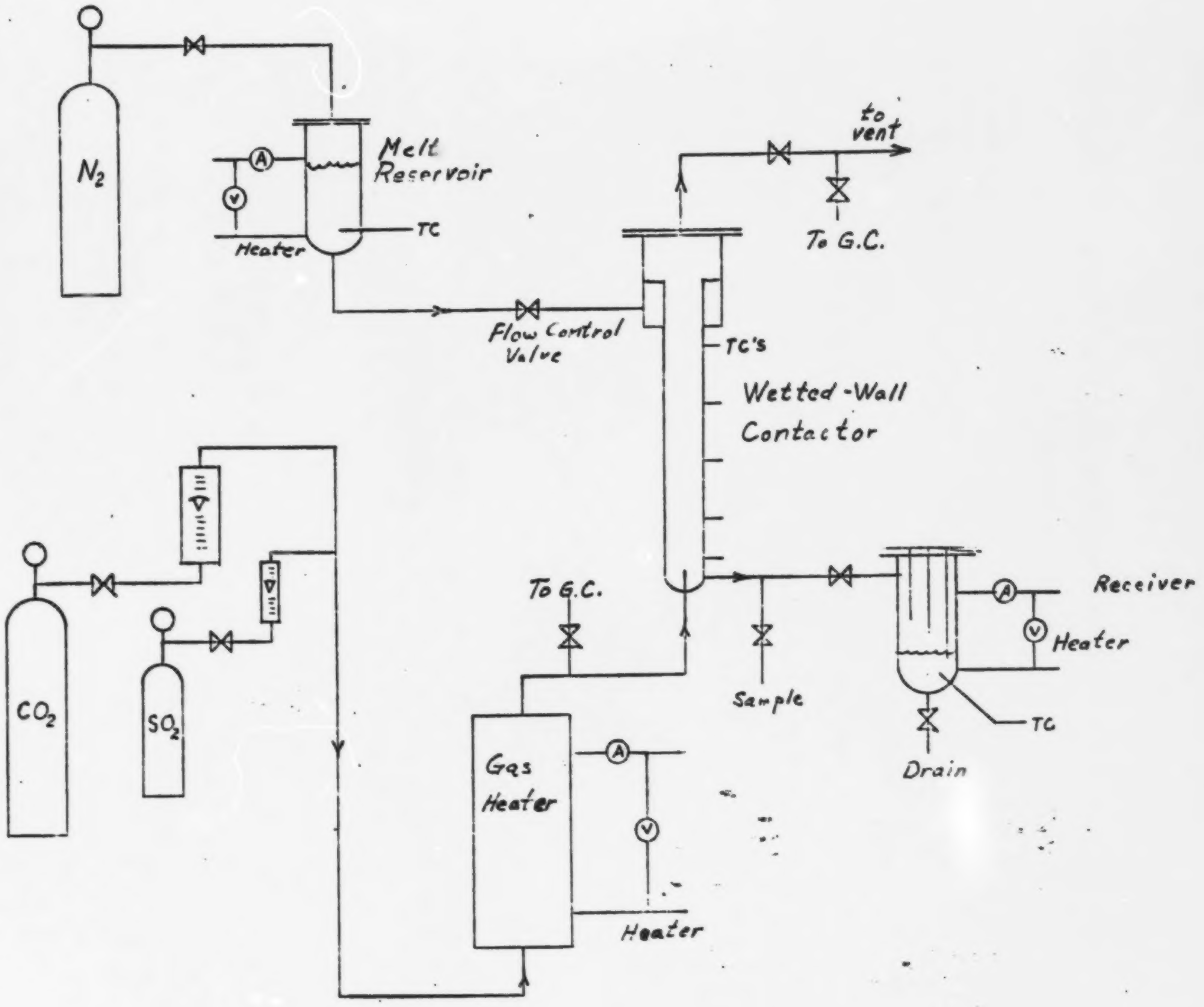

N₂
Melt Reservoir
A
V
Heater
TC
Flow Control Valve
to vent
To G.C.
TC's
Wetted-Wall Contactor
CO₂
SO₂
To G.C.
Gas Heater
A
V
Heater
Sample
Receiver
A
V
Heater
TC
Drain

Figure 30. Contactor Test Stand

The first scrubber contactor tests were done with a wetted-wall contactor; later, a baffled-tube contactor was tested and nozzles for a spray chamber were also studied.

b. Wetted-Wall Contactor Tests

The wetted-wall contactor was made of a 24-in. long section of 1-in. diameter type 347 stainless steel tube, provided with a melt distribution weir at the top and a gas inlet and melt outlet at the bottom. It is shown schematically as the contactor in Figure 30. Tests were performed with this contactor primarily to determine if the mass transfer in scrubber contactors was gas-film limited or not, and also to measure the mass transfer coefficient. A total of 32 tests were carried out, over the range of operating conditions listed in Table 45.

TABLE 45

WETTED WALL CONTACTOR TEST CONDITIONS

Gas Flow Rate	25-250 scfh
Gas Velocity	2.75-30.8 ft/sec
Reynolds Number	580-5360
Gas Temperature	660-850°F
Salt Flow Rate	1-6 lb/hr
Salt Temperature	840-900°F
Inlet SO_2 Concentration	0.1-0.61 vol %

During each test, the sulfur dioxide concentration in the inlet and exit gas streams was measured with a gas chromatograph, and the results used to calculate the mass transfer coefficient for the column. The test conditions and mass transfer coefficients are listed in Table 46.

There is a great deal of scatter in the data; this must be attributed in large part to inaccuracy in measuring the change in the sulfur dioxide concentrations of the inlet and exit gas streams, and also in measuring

TABLE 46

ONE INCH DIAMETER WETTED WALL CONTACTOR TEST RESULTS

Carrier Gas Flow (SCFM-CO_2)	Gas Temp. (°F)	Salt Flow (lb/hr)	Salt Temp. (°F)	SO_2 Concentration		Gas Velocity (ft/sec)	Mass Flow Rate G (lb/hr ft^2)	Reynolds Number	k_G $\left(\frac{\text{lb moles}}{\text{hr/ft}^2\text{ atm.}}\right)$
				Inlet (vol. %)	Outlet (vol. %)				
25	715	1.85	880	0.23	0.12	2.75	510	585	0.0825
25	715	1.85	880	0.25	0.125	2.75	510	585	0.0882
25	715	1.85	880	0.22	0.12	2.75	510	585	0.077
25	735	1.06	895	0.605	0.395	2.8	510	580	0.056
25	735	3.7	895	0.61	0.39	2.8	510	580	0.057
40	750	2.8	880	0.30	0.25	4.55	820	920	0.037
40	700	1.85	840	0.30	0.215	4.35	820	950	0.067
40	720	3.7	888	0.30	0.205	4.35	820	935	0.077
45	790	5.8	850	0.37	0.23	5.3	920	1000	0.11
45	670	1.06	870	0.34	0.11	4.8	920	1075	0.257
45	790	5.8	850	0.10	0.071	5.3	920	1000	0.078
50	800	1.06	875	0.59	0.26	5.9	1020	1100	0.21
72	750	2.8	885	0.265	0.175	8.2	1475	1660	0.156
75	750	2.8	885	0.245	0.20	8.6	1540	1720	0.077
80	750	1.85	885	0.215	0.15	9.1	1640	1835	0.153
80	755	1.85	885	0.228	0.18	9.15	1640	1825	0.095
80	720	3.7	888	0.30	0.23	8.9	1640	1870	0.11
80	835	1.9	850	0.21	0.08	9.75	1640	1730	0.395
90	790	5.8	850	0.095	0.06	10.6	1845	2010	0.21
95	660	1.06	865	0.14	0.065	10.0	1945	2340	0.371
100	750	1.39	890	0.45	0.265	11.35	2045	2300	0.268
100	750	1.85	896	0.45	0.26	11.35	2045	2300	0.28
115	760	1.06	868	0.22	0.11	13.25	2345	2620	0.41
120	750	2.8	880	0.24	0.198	13.7	2460	2750	0.11
152	750	1.85	900	0.27	0.20	17.35	3110	3480	0.22
153	760	1.85	880	0.30	0.23	17.45	3130	3480	0.21
153	760	1.85	880	0.135	0.09	17.45	3130	3480	0.31
173	820	1.85	860	0.20	0.13	19.15	3540	3770	0.38
190	840	1.85	860	0.175	0.13	21.4	3890	4100	0.28
200	830	1.85	870	0.195	0.055	24.3	4090	4350	1.1
200	850	1.85	880	0.19	0.13	24.7	4090	4300	0.39
250	850	1.85	880	0.20	0.13	30.8	5120	5360	0.54

the total gas flow rates. These difficulties, in turn, were largely caused by the very short contact times in the column. Because of their scatter, these data have little value as engineering values for designing larger wetted-wall contactors. However, the data are quite significant in that they show no dependence of the mass transfer coefficient on the melt flow rate. This is a good indication that the mass transfer is gas-film controlled, as expected. If a significant portion of the mass transfer resistance were in the liquid film, doubling the liquid flow rate would cause a marked increase in the mass transfer coefficient. Instead, the test results show that increasing the liquid flow rate by a factor of 2 to 5 caused no consistent change, within the scatter of the data.

For comparative purposes, two of the standard correlations for predicting gas-film-limited mass transfer in wetted wall columns(6) were compared with the experimental data; i.e.,

Gilliland Correlation:

$$\frac{k_G RTD}{D_v} \frac{P_{BM}}{P} = 0.023\ Re^{0.83}\ Sc^{0.44} \qquad (22)$$

Chilton-Colburn Correlation:

$$\frac{k_G P_{BM}}{G_M} Sc^{2/3} = \frac{f}{2} \qquad (23)$$

(The nomenclature is given in Appendix D)

Both correlations fall within the scatter of the experimental data.

c. Baffled-Tube Contactor Tests

A 2-in. diameter baffled tube was also tested as a scrubber contactor. It is shown schematically in Figure 51. The melt entered at the top and dripped down through the contactor, flowing across the top of each of the ten baffles and keeping their surfaces wetted. This provided for more mass transfer area than in a wetted-wall column of similar length. Also, as the gas stream passed up through the column the baffles increased the gas turbulence, leading to enhanced mass transfer.

The first tests were done using mixtures of sulfur dioxide and carbon dioxide, to study the removal efficiency. Thirteen tests were performed, with the results summarized in Table 47. These data show that the baffled-tube contactor was quite efficient, since at least 92% of the sulfur dioxide was removed in each test.

In 7 of the tests, no sulfur dioxide could be detected in the exit gases. In these cases, the exit concentration was less than 0.005% (50 ppm), since this was estimated to be the lower limit which could be measured with the gas chromatograph.

The height-of-a-transfer-unit values (HTU's) of Table 47 were calculated from the relationship

$$\mathrm{HTU} = \frac{h}{\ln\left(\frac{C\ \mathrm{in}}{C\ \mathrm{out}}\right)} \tag{24}$$

These values were all between 6 and 10 inches, much less than the 40-80 inches estimated for a wetted-wall column of the same diameter.

It was also observed that the ability of this contactor to remove sulfur dioxide was independent of the melt flow rate. As an illustration

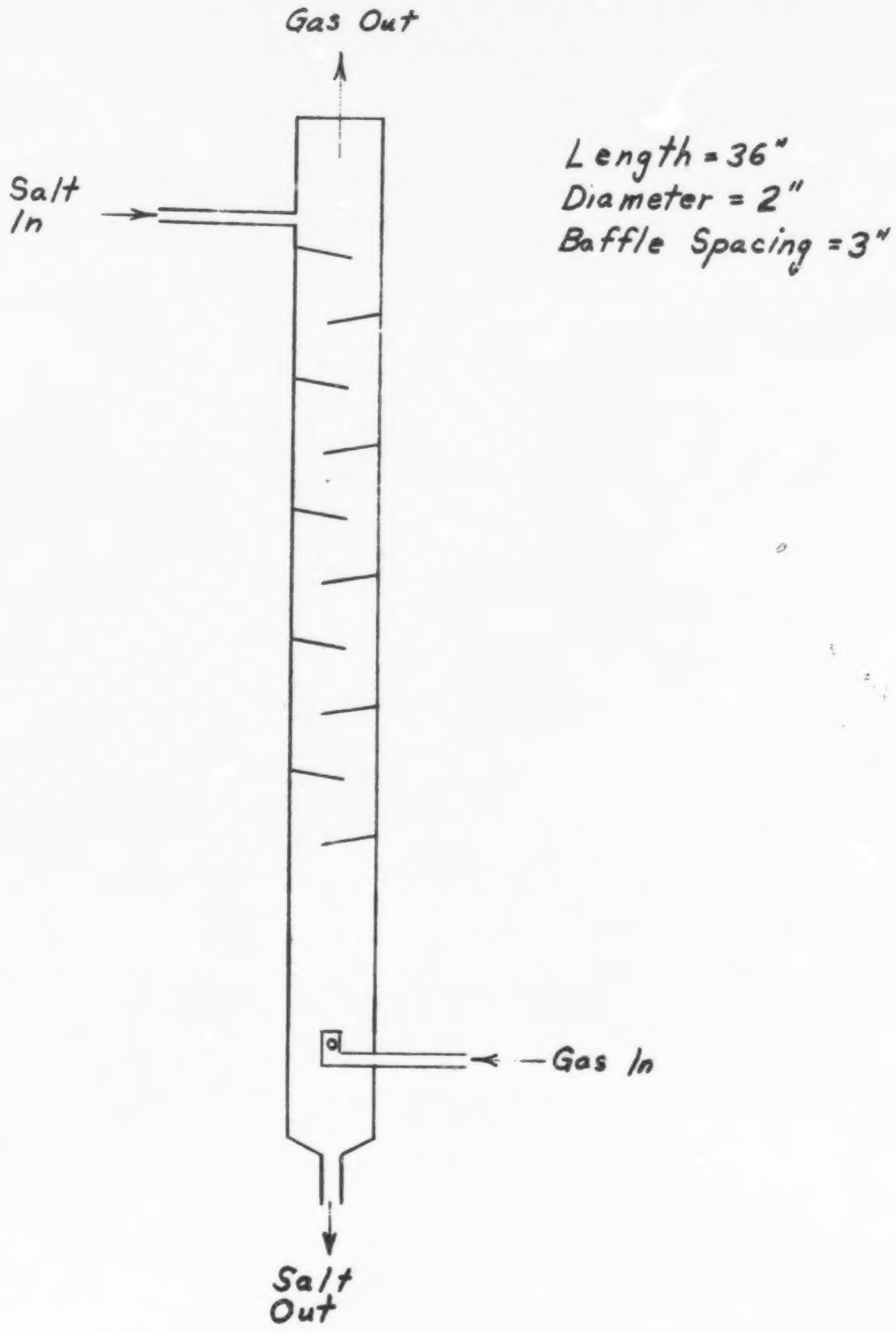

Gas Out
Salt In
Length = 36"
Diameter = 2"
Baffle Spacing = 3"
Gas In
Salt Out

Figure 31. Baffled-Tube Contactor

TABLE 47

BAFFLED-TUBE CONTACTOR TEST RESULTS

Gas Flow Rate (scfh) (CO_2 + SO_2)	Temp (°F)	ΔP (in. H_2O)	SO_2 Concentration		SO_2 Removal Efficiency (%)	N_{Re}[b]	HTU (in.)
			Inlet (vol %)	Outlet (vol %)			
30.51	805	0.14	1.54	0.12	92	325	10.5
30.51	805	0.14	1.54	0.08	95	325	9.1
30.25	815	0.14	0.92	0.035	96	325	8.3
50.50	900	-	1.00	N.D.[a]	99+	540	5.1
55.16	940	-	0.36	N.D.	99	580	6.3
55.30	900	-	0.62	N.D.	99	595	5.6
61.50	900	0.325	0.82	0.065	92	664	10.5
60.25	815	0.325	0.44	0.02	95	688	8.7
60.25	815	0.325	0.44	0.02	95	688	8.7
120.51	950	1.7	0.38	N.D.	99	1270	6.3
120.51	770	1.7	0.38	N.D.	99	1400	6.3
120.25	925	1.7	0.21	N.D.	98	1280	7.1
160.51	790	4.0	0.27	N.D.	98	1830	6.8

[a] SO_2 not detectable

[b] Based on unbaffled flow area

of this, in one test the melt flow rate was stopped completely, so that all the sulfur dioxide removal was by residual melt remaining in the column. When this was done, the removal efficiency remained unchanged (in this case at greater than 99%) for over 15 minutes. This further verifies that the mass transfer is gas-film controlled.

The pressure drops measured during the tests were quite high, and probably make this particular contactor design unsuitable for scaling up to pilot plant size. The highest gas flow rate tested (160 scfh) corresponded to a linear gas velocity in the unbaffled part of the tube of only 4.85 ft/sec, and at this flow rate the pressure drop was 4 in. of water. The pilot plant contactor should have no higher pressure drop with about five times the gas flow rate. Contactors with lower pressure drops will be tested in the near future.

The experimental HTU values can be used to estimate the lengths of baffled-tube contactors for a commercial installation or pilot plant. For 95% removal efficiency, 3 transfer units or 30 inches would be needed, while 99% removal efficiency would require 5 transfer units or only 50 inches. These would be short, quite efficient units.

d. Nitric Oxide Effects

The baffled-tube contactor of Figure 31 was also used in tests to study the effect of nitric oxide (NO) on the rate of removal of sulfur dioxide. To do this, provision was made for adding nitric oxide to the carbon dioxide and sulfur dioxide inlet gases, and the gas chromatograph was modified to increase its sensitivity to sulfur dioxide and nitric oxide. The detection limits were estimated to be 20 ppm of SO_2 and 10 ppm of NO.

Five tests were performed, with inlet nitrogen oxide concentrations varying from 220 to 1340 ppm. The conditions and results are tabulated in Table 48.

The sulfur dioxide results merely confirm the previous tests, in that greater than 99% removal occurred in each test. The nitric oxide removal efficiency was much lower, however, being 32% or less for all but one test. This indicates that the absorption rate of nitric oxide is much slower than that of sulfur dioxide, at least under the test conditions. This is presumably because the chemistry of the absorption reaction is more complex. The absorption of sulfur dioxide proceeds by a simple acid-base reaction (reaction 1), while nitric oxide cannot react directly with the molten carbonate. Instead, a redox reaction must first occur to oxidize the nitric oxide to a more reactive species, which will then react with the carbonate. The reaction mechanisms are thus much more complicated than the simple sulfur dioxide absorption reaction, and probably contain one or more rate-limiting chemical reaction steps, whereas the rate-limiting step in the sulfur dioxide absorption is diffusion in the gas phase.

It should be noted that the nitric oxide absorption tests were done in the absence of oxygen, so that a redox reaction involving oxygen could not occur. Because of this, the absorption rate from actual flue gases (containing ~ 5% oxygen) may be higher. Nitric oxide absorption tests in the presence of oxygen are planned for the near future.

It should also be noted that the data indicate there may be a slight improvement in nitrogen oxide absorption due to the presence of the sulfur dioxide. However, much more data is needed to support such a conclusion.

TABLE 48

BAFFLED-TUBE CONTACTOR TEST RESULTS WITH NITRIC OXIDE

(Melt Flow = 4.9 lb/min)

Gas Flow Rate (scfh) (CO_2 + SO_2 + NO)	Temp (°F)	SO_2 Concentration		NO Concentration		Removal Efficiency		HTU	
		Inlet (ppm)	Outlet (ppm)	Inlet (ppm)	Outlet (ppm)	SO_2 (%)	NO (%)	SO_2 (in.)	NO (in.)
50.18	850	2980	N.D.*	450	220	99.5	51	5.4	38
50.16	870	2900	N.D.	220	150	99.3	32	5.4	70
60.04	870	0	0	590	400	-	32	-	70
60.28	910	3540	N.D.	1340	1050	99.5	22	5.2	111
75.24	885	2400	N.D.	530	385	99.1	29	5.6	84

*N.D. = not detectable

No effect of nitric oxide on the absorption of sulfur dioxide could be detected, but the removal efficiency was so high that slight effects may have been masked. Certainly the nitric oxide did not cause any significant decrease in the sulfur oxide absorption rate.

e. Spray Tower Tests

The first spray tower tests were attempted in a vertically-mounted 2-in. diameter chamber approximately 2 ft long. This had a single spray nozzle located in the center at the top, installed to spray melt downward into an upward flowing gas stream.

Initial tests were made with a commercial open-cone type nozzle. These were unsuccessful, evidently due to plugging of the very small orifice required to spray at low melt flow rates. This nozzle was then modified to enlarge the flow passages, and retested. Operation of the modified nozzle was achieved, but at a melt flow rate which was an order of magnitude too high. Because of the high flow rate, the melt reservoir emptied before steady-state conditions could be achieved, and test data could not be obtained.

An aspirator-type nozzle, in which a gas stream was used to atomize the salt into a spray, was then designed and built. This nozzle was put into operation, at low melt flow rates. The spray it produced was a very fine mist, some of which was blown out of the top of the spray tower by the gas stream.

Analytical studies have shown that effective mass transfer can be obtained in this small spray tower only when the drop sizes are controlled within very narrow limits. Because of this, a larger spray chamber has been designed and is now being built. This chamber is 6 in. in diameter, and is provided with a sight glass for observation of the nozzle operation.

2. Reducer Contactor Development

A second contactor test stand has been built, for testing reduction contactors. It is similar to the test stand of Figure 30, but has a larger melt reservoir and receiver, and also a melt return line from the receiver to the reservoir. Therefore, it will be possible to recycle the melt being treated, by periodically forcing the melt from the receiver back into the reservoir with nitrogen gas. The first reducer contactor to be tested will be a 3-in. diameter column packed with 1/4-in. graphite raschig rings.

D. COMPONENT DEVELOPMENT

The component development work has concentrated on fly ash filtration. A filter test device was built for this. The filter medium was a sintered stainless steel disc, sealed inside a tube so that gas pressure could be used to force salt through it. Seventeen different filtration tests were performed, with the results summarized in Table 49.

The filtrate from Run No. 4 was analyzed spectroscopically for silica and alumina, and found to contain only 0.20 and 0.22%, respectively. From this and the other results listed in Table 49, it appears that the fly ash is not rapidly soluble in the molten carbonate eutectic, and can be removed by filtration. Samples of filtrate from other runs have been submitted for analysis for iron, calcium, magnesium, and other fly ash constituents as well as for silica and alumina. These data will be reported as soon as they are available.

In the majority of the above tests, most of the melt passed through the filter media within one minute after the pressure was applied. However, it appears that filtration will also cause the removal of a substantial amount of carbonate, due to retention of melt in the cake. This will be studied

TABLE 49

FLY ASH FILTRATION TEST RESULTS

Run	Pore Diam (μ)	Ash Content (grams ash in 90 grams Carbonate)	Temp (°F)	Time (min)	Pressure (psig)	Filtrate Wt and Analysis
1	25	4.5	900	5	10	82.7 gm No ash
2	25	9.0	875	20 5	0 10	52.6 gm No ash
3	25	9.0	850	10	10	62 gm No ash
4	25	9.0	860	30	20	78 gm 99% M_2CO_3
5	25	9.0	850	--	30	Filter ruptured
6	35	9.0	850	30	10	75 gm, no fly ash
7	35	9.0	880	30	20	77.1 gm 98.1% M_2CO_3
8	35	9.0	860	30	20	66.3 gm 92.9% M_2CO_3
9	35	9.0	860	5	20	68.8 gm No ash
10	35	9.0	860	10	20	72.6 gm No ash
11	35	9.0	875	30	0	26.1 gm No ash
12	35	9.0	875	1	20	72.5 gm 99.7% M_2CO_3
13	35	9.0	860	1	20	73.5 gm No ash
14	35	9.0	860	5	20	70 gm No ash
15	65	9.0	840	1	20	74 gm 98.1% M_2CO_3
16	65	9.0	870	10	20	75.1 gm 99.47% M_2CO_3
17	65	9.0	850	5	20	69 gm No ash

Runs 14 and 17 were done with fly ash from Consolidation Coal Co. The rest were done with fly ash received from the NCAPC laboratory at Cincinnati, Ohio. **Analyses are given in Appendix B.**

further, in future tests with other fly ash samples. An attempt will be made to characterize the cake which can be expected from a continuous fly ash filter.

Tests will also be done using a deep bed type filter, made of charcoal granules.

Fly ash samples have been received from the following sources:

(1) NCAPC, Cincinnati

(2) Consolidation Coal Co.

(3) Arizona Public Service Co., Four Corners Station

(4) Arizona Public Service Co., Cholla Station

(5) Los Angeles Dpt. of Water and Power (oil soot)

(6) Northern States Power Co., Minneapolis; Riverside Station

(7) Northern States Power Co., Minneapolis; Black Dog Station

(8) Public Service Co. of Colorado; Cherokee Station

(9) Public Service Co. of Colorado; Arapahoe Station

E. PILOT PLANT AND COMPONENT TEST LOOP DESIGN

Conceptual design studies of a small pilot plant and a component test loop have been initiated, and are now underway. Preliminary flow diagrams of both units have been prepared, and very approximate cost estimates have been made. Work is now proceeding on detailed flow diagrams and engineering arrangement drawings, and on sizing and specifying equipment and components.

The small pilot plant will be operated to test the process and its chemistry on a continuous basis, and to study the possible build-up of trace impurities with time. It will use the flue gases from an actual coal-burning furnace. The preliminary flow diagram for this pilot plant is shown in Fig. 32.

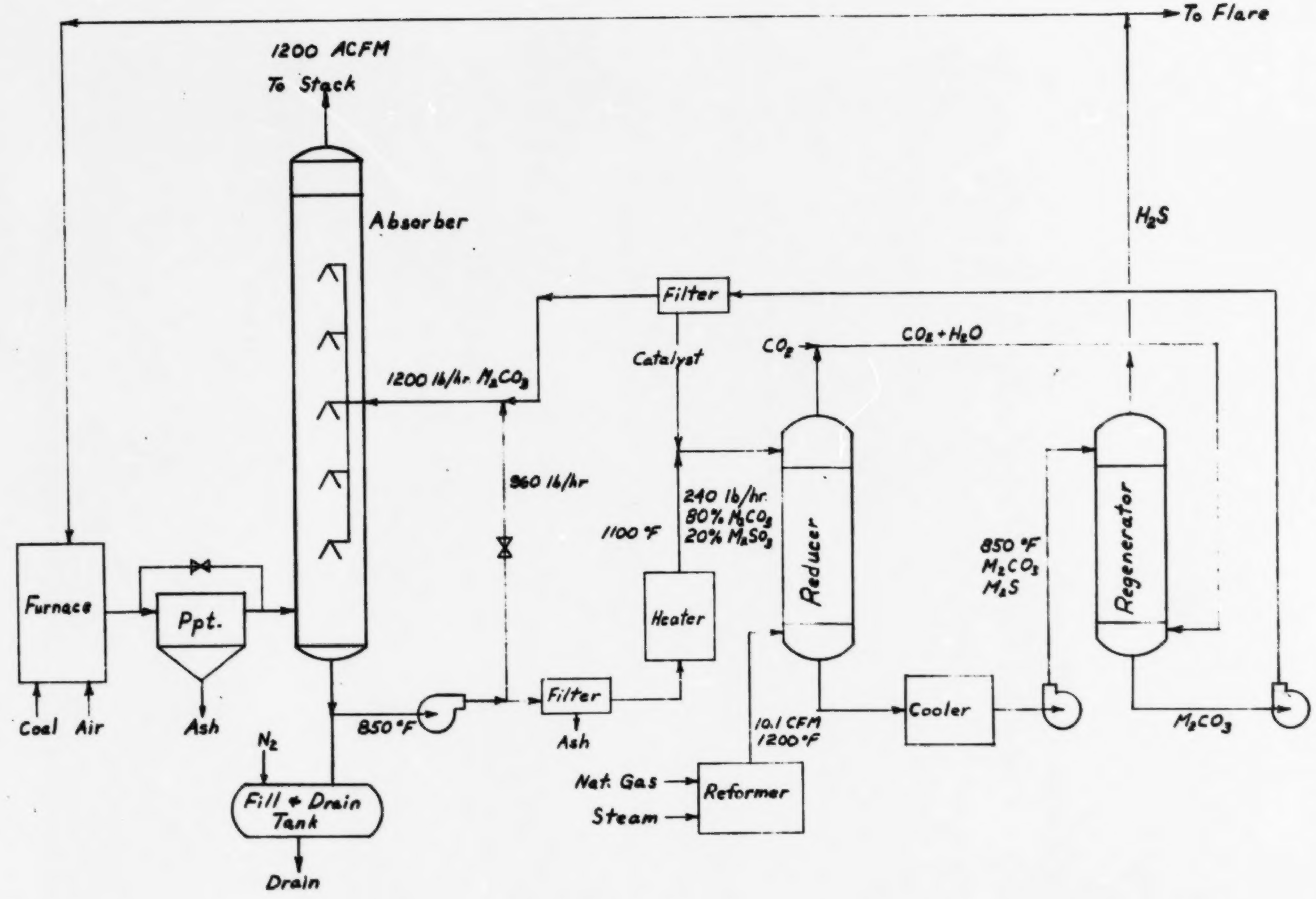

To Flare
1200 ACFM
To Stack
Absorber
H_2S
Filter
$CO_2 + H_2O$
CO_2
Catalyst
1200 lb/hr. M_2CO_3
960 lb/hr
240 lb/hr.
80% M_2CO_3
20% M_2SO_3
1100 °F
850 °F
M_2CO_3
M_2S
Furnace
Ppt.
Heater
Reducer
Regenerator
Coal
Air
Ash
N_2
850 °F
Filter
Ash
Fill + Drain Tank
Drain
10.1 CFM
1200 °F
Cooler
M_2CO_3
Nat. Gas
Steam
Reformer

Figure 32. Pilot Plant Flow Diagram

The coal-burning furnace will be similar in design and capacity to the furnace built by the Bureau of Mines for the Alkalized Alumina Process pilot plant.(7) The pilot plant components will be sized to treat the gases from this furnace. The scrubber contactor shown is a spray tower, with a gas throughput velocity of about 8 ft/sec. The reducer and regenerator are shown as identical packed columns, with one-hour melt holdup capacities. Estimates of the sizes of the other items and the process stream flow rates are also given in the figure. This arrangement is now being re-examined in detail, and it is possible that the types and sizes of most of the components will be changed in the final pilot plant design. A very approximate cost estimate for the small pilot plant yielded an installed cost of about $386,000 plus the cost of the coal-burning furnace.

The small pilot plant melt flow rate to the regenerator is only 240 lb/hr, or 1/4 gal./min. This flow rate is too slow for the effective testing of the thermal and hydraulic components of a prototype unit. Because of this, a component test loop will be built and operated, with a melt flow rate of 25 gal./min. This will be the approximate throughput of a 100 Mw(electrical) unit, and will make possible the full-size testing of pumps, valves, flow meters, heaters, and heat exchangers. Fly ash effects and fly ash removal systems will also be tested with this unit. The preliminary flow diagram is shown as Figure 33. A very approximate cost estimate for this unit, installed, was $542,000.

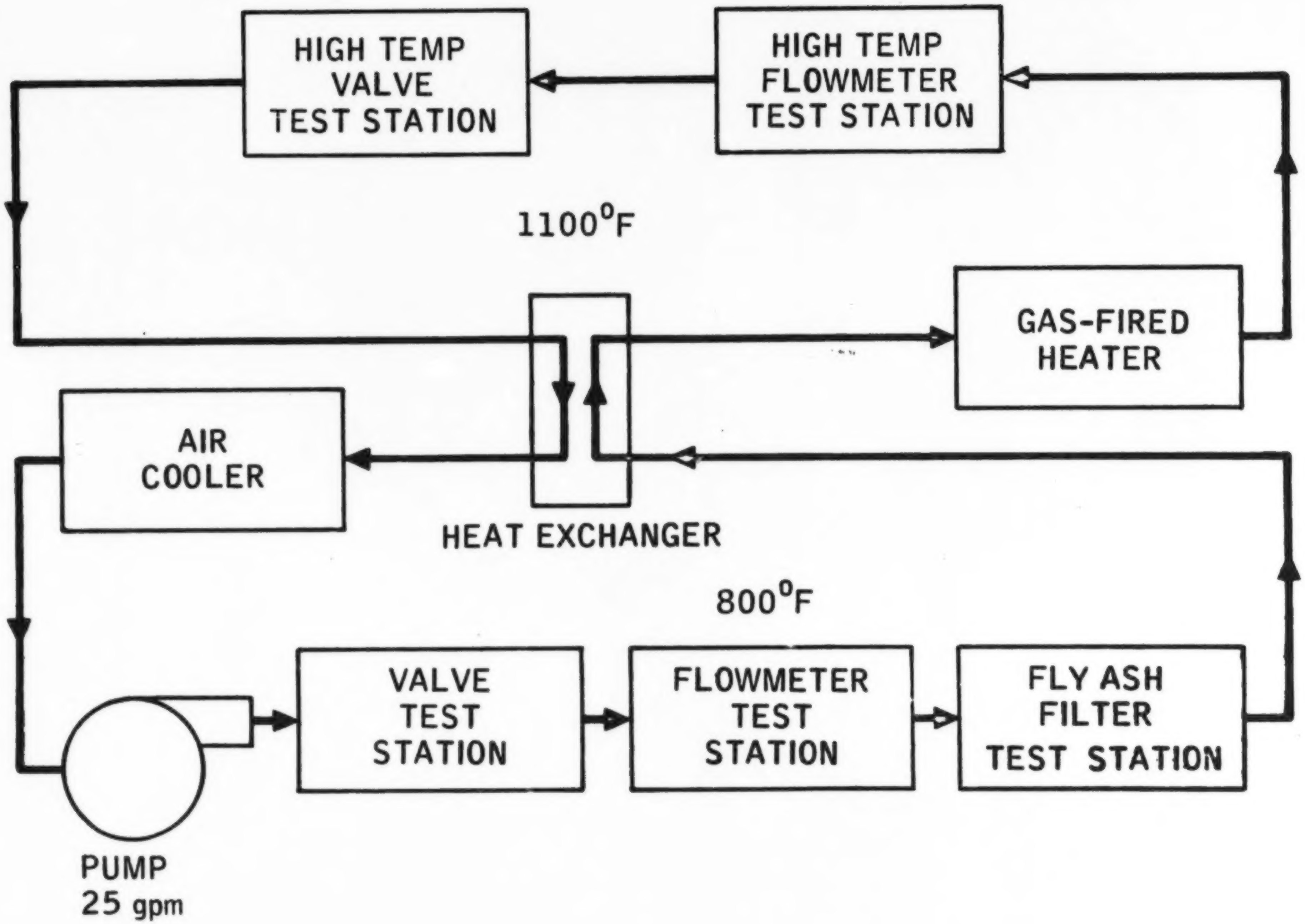

HIGH TEMP VALVE TEST STATION
HIGH TEMP FLOWMETER TEST STATION
1100°F
GAS-FIRED HEATER
AIR COOLER
HEAT EXCHANGER
800°F
VALVE TEST STATION
FLOWMETER TEST STATION
FLY ASH FILTER TEST STATION
PUMP
25 gpm

Figure 33. Component Test Loop Flow Diagram

III. PRESENT STATUS

The results described in the previous section have added greatly to the understanding of the molten carbonate process, and make it possible to describe a "Reference Process" which is both technically feasible and economically attractive. The present status of each major development project is described below; the Reference Process is defined and described in the next section.

A. PROCESS CHEMISTRY

1. Absorption

The absorption tests showed that the absorption reaction was very rapid and that oxygen, water vapor, and fly ash would not interfere with removal of the sulfur oxides by the molten carbonate. It was also found that some of the sulfite formed was oxidized to sulfate, the amount depending on contact time and oxygen content of the flue gas. Tests with combustion gases showed that large amounts of excess oxygen would oxidize sulfide and sulfite in the melt to sulfate, and that hydrogen sulfide would not be emitted from the melt even when sulfides were contacted with moist flue gases. The tests thus showed that the carbonate melt was an excellent absorbent under realistic conditions, with a very fast reaction rate. The main problem involved in the absorption process is then to bring the sulfur oxides into contact with the carbonate melt.

2. Reduction

Recent reduction studies have concentrated on catalysis. Iron and tin compounds have been found to increase the rate of the reduction reaction, and a reduction reaction mechanism has been proposed which may lead to other catalysts. Reduction rates under process conditions will have to be determined in tests combining catalysis with optimum gas-liquid mass transfer. However, it is expected that the results of preliminary tests, indicating 1 hour would be required at 1100°F, may be improved upon somewhat. Catalysis studies will continue, including studies to determine how best to carry out the catalyzed reductions and how to keep the catalyst in the reactor.

3. Regeneration

Regeneration tests have shown that the melts can be regenerated to carbonate for recycling to the scrubber, and that the sulfur can be recovered as hydrogen sulfide with good efficiency. However, indications have been found that the reduction catalysts cause foaming problems during regeneration, and also tie up some of the sulfur. The foaming may be eliminated by carrying out the regeneration reaction in large surface area reactors, and the sulfur tie-up may not occur after the catalyst is saturated. Further studies, including cycle tests, will be performed to study these effects.

B. CORROSION STUDIES

Screening tests have been completed for most practical metals and alloys, and certain candidates have been selected for long-term tests. Long-term tests of type 347 stainless steel have shown it to be suitable for use at 950°F with any melt, but unsuitable with melts containing sulfide or sulfite at 1110°F, the reference process reduction temperature. Several alloys appear suitable for this service; they are now being tested. Many nonmetallic materials have also been given screening tests, and graphite, alumina, magnesia, and zirconia have been found to warrant further study.

Long-term testing will continue, and the effects of water, fly ash, reducing gases, and other impurities on corrosion rates will be investigated.

C. CONTACTOR DEVELOPMENT

Wetted-wall column and baffled-tube contactor tests have been performed. The results show that mass transfer in the scrubber contactor is gas-film controlled. This knowledge makes it possible to estimate the performance of other types of scrubbers more suitable for large scale use. The scrubber contactor must treat large volumes of flue gas with a low pressure drop. This can probably be done in a spray tower or a tray-filled chamber.

The baffled tube contactor was very efficient, and removed more than 97% of the sulfur dioxide from the test gas streams with only 36 in. of contact. However, it had a high pressure drop.

Tests with nitric oxide and sulfur dioxide in the baffled tube contactor showed that the nitric oxide was also absorbed, but that about ten times as much contactor length was required as for the sulfur dioxide. This will be studied further with more realistic gas mixtures, including oxygen, which may enhance the nitric oxide absorption rate.

Spray nozzle tests have shown that both regular open cone and aspirator type nozzles can be used; however, the test equipment was not large enough for measurements to be made of mass transfer rates to the sprayed droplets. Other types of scrubber contactors remain to be tested, as do packed column and tray column contactors for the reduction and regeneration steps. A packed column reducer contactor is now being prepared for testing.

D. COMPONENT DEVELOPMENT

Component development work concentrated on fly ash filtration, since this was an obvious need. Preliminary indications were that the fly ash was virtually insoluble in the carbonate melt, and could be removed with a sintered stainless steel filter. However, further study is needed of this, and to predict the performance of a continuous filter.

Development of pumps, valves, and other components has awaited determination of suitable materials of construction. No particular design problems are envisioned.

E. PILOT PLANT AND COMPONENT TEST LOOP DESIGN

Conceptual design studies of these units have been initiated, and preliminary flow diagrams have been prepared. This work is continuing, with work on detailed flow diagrams and engineering arrangement drawings now underway.

IV. THE REFERENCE PROCESS

The process development work completed makes it possible to describe and evaluate a reference molten carbonate process. This reference process is not in optimum or final form, but its feasibility has been demonstrated.

The flow diagram of the reference process is that shown in Figure 34. This flow diagram was prepared before the most recent reduction and regeneration test results were available; further testing may show that it must be modified to include a catalyst filter and return line downstream of the reducer or regenerator. However, this is still uncertain, as are the reduction and regeneration time requirements. It would probably be inefficient to make revisions until more information becomes available. Until then, the reference process will be considered to be that shown in Figure 34, with the following specific features:

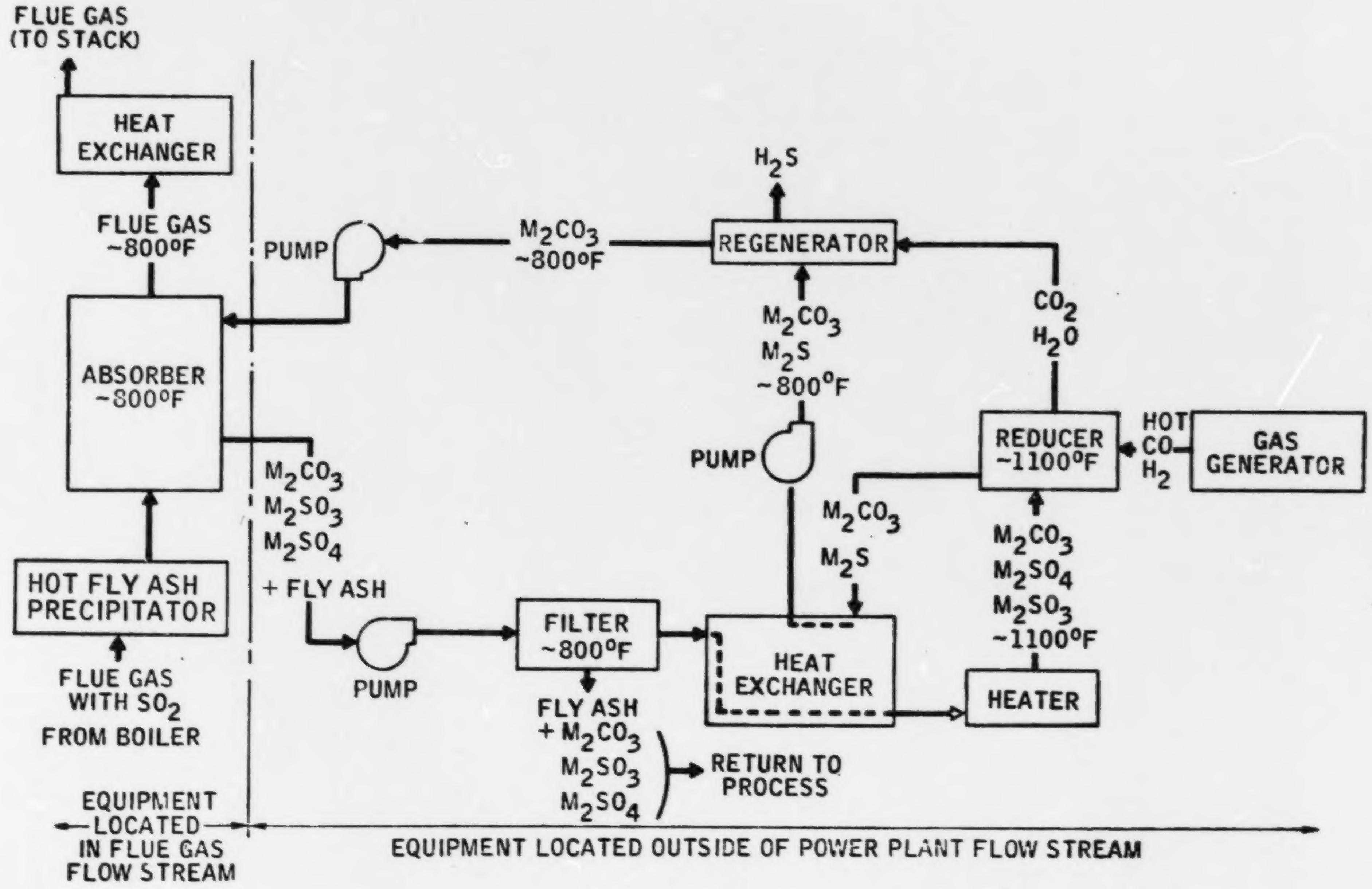

FLUE GAS
(TO STACK)
HEAT EXCHANGER
FLUE GAS
~800°F
ABSORBER
~800°F
HOT FLY ASH PRECIPITATOR
FLUE GAS
WITH SO_2
FROM BOILER
PUMP
M_2CO_3
~800°F
REGENERATOR
H_2S
M_2CO_3
M_2S
~800°F
CO_2
H_2O
REDUCER
~1100°F
HOT
CO
H_2
GAS GENERATOR
M_2CO_3
M_2SO_3
M_2SO_4
+ FLY ASH
PUMP
PUMP
FILTER
~800°F
FLY ASH
+ M_2CO_3
M_2SO_3
M_2SO_4
RETURN TO PROCESS
HEAT EXCHANGER
M_2CO_3
M_2S
HEATER
M_2CO_3
M_2SO_4
M_2SO_3
~1100°F
EQUIPMENT LOCATED IN FLUE GAS FLOW STREAM
EQUIPMENT LOCATED OUTSIDE OF POWER PLANT FLOW STREAM

Figure 34. Reference Process Flow Diagram

(1) The flue gas is removed from the boiler at ~ 800°F, and passed through a high-temperature fly ash precipitator where 95% of the fly ash is removed. It then passes through the scrubber where it is contacted with molten carbonate, also at 800°F. The scrubbing process removes 95% of the sulfur oxides and all the remaining fly ash from the gases. The cleaned gases are then returned to the boiler, from whence they pass eventually to the stack.

(2) The carbonate stream, containing approximately 20% sulfite and 15% sulfate, is pumped to a filter and filtered to remove the fly ash. About 85% of the salt removed as filter cake is recovered and returned to the process.

(3) The filtered melt is heated from 800°F to 1100°F in a regenerative heat exchanger and heater, and then fed into the reducer. Here the sulfite and sulfate are completely reduced to sulfide in one hour of contact, using producer gas. An excess of 10% gas is supplied, with the reaction using 80% of the hydrogen and 20% of the carbon monoxide.

(4) The salt stream from the reducer is passed through the regenerative heat exchanger and cooled to ~ 800°F. It then is pumped to the regenerator and contacted with the carbon dioxide and water produced in the reduction step. Complete regeneration is accomplished in about 15 minutes, and the sulfur is removed as hydrogen sulfide and supplied to a Claus-process sulfur plant.

(5) The regenerated melt is recirculated to the absorber, with the small losses in the filter cake being made up by addition of fresh carbonate.

A preliminary economic evaluation of this reference process was performed, using the method described by Katell.(8) The results, for an 800-Mwe installation, were a capital requirement of $\$8.208 \times 10^6$ ($10.25/kw) and an annual operating cost, with a 90% load factor, of $\$2.878 \times 10^6$/year (0.454 mills/kw-hr). These values indicate that the reference molten carbonate process is competitive with the other processes presently under development.

V. REFERENCES

1. von Fredersdorff, C. G., and M. A. Elliott; "Coal Gasification," in "Chemistry of Coal Utilization," Supplementary Volume, H. H. Lowry, Editor, New York, John Wiley and Sons, Inc., 1963 p. 952
2. Budnikov, P., and E. Shilov, J. Soc. Chem. Ind., 47, 111 (1928)
3. Nikitin, V. A., and T. I. Kunin, Chem. Abstracts, 59:9614h (1963)
4. Nyman, C., and T. O'Brien, Ind. and Eng. Chem., 39, 1019 (1947)
5. Janz, G. J. and A. Conte, Electrochemica Acta, 9, 1279 (1964)
6. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," New York, McGraw-Hill Book Co., Inc., 1952
7. Kurtzrock, R. C., D. H. McCrea, and G. J. Cinquegrane, "Designing an Alkalized Alumina Pilot Plant for Sulfur Oxides Removal," Paper for presentation at TMS Operating Metallurgy Conference, Chicago, Ill., December 11-15, 1967
8. Katell, S., Chemical Engineering Progress, 62 (10) 67 (Oct. 1966)

APPENDIX A. ANALYTICAL PROCEDURES

I. GAS CHROMATOGRAPHIC DETERMINATION OF SULFIDE, SULFITE, AND CARBONATE IN SOLIDIFIED MELT SAMPLES

A rapid, sensitive, and reasonably accurate gas chromatographic technique has been developed for the determination of sulfide, sulfite, and carbonate in solidified salts. Seventy-five percent sulfuric acid is added to the salt which is contained in a closed evacuated system. The resulting reaction of the respective salts with the acid to form hydrogen sulfide, sulfur dioxide, and carbon dioxide is rapid and quantitative. A measured portion of these evolved gases is separated by a gas chromatographic column packed with porous polymer beads, and is then analyzed using a thermal conductivity detector. Samples weighing only 0.1 gram and containing as little as 1% sulfite and/or sulfide in fused alkali carbonate can be analyzed with 6% accuracy with respect to sulfide and sulfite and 2% accuracy with respect to carbonate. Total analysis time is less than 6 minutes.

Apparatus. A Loenco model 15A gas chromatograph in conjunction with a thermal conductivity detector is used. The column, of "Porapac Q" is 6 ft x 1/4 in. and is operated at 100°C with a helium flow rate of 60 cc/min.

Standardization. Standards are prepared by carefully mixing and weighing several concentrations of mixed alkali metal sulfide, sulfite, and carbonate, fusing the mixtures, and then drawing the fused salt mixtures up into 5 mm quartz tubes. The standards are then analyzed by wet chemistry to verify concentrations and then used to standardize the gas chromatograph.

Procedure.

1. Weigh out 70 to 90 gm samples and place in the reaction vessel. Evacuate the system.
2. Close the reaction vessel valve and add 1.0 ml 75% H_2SO_4. After dissolution, heat the solution at 200°C for 1 min.
3. Close the vacuum valve, open the reaction vessel valve, and place a 5.0 ml portion of this total gas volume (81.9 ml) in the carrier-gas stream by means of a Perkin-Elmer sampling valve.
4. Retention times for air, CO_2, H_2S, and SO_2 are 40, 61, 155, and 316 seconds, respectively.

II. DETERMINATION OF SULFATE IN ALKALI METAL CARBONATES

The procedure used in our [illegible]tory for the determination of sulfate is the classical approach which depends upon the insolubility of $BaSO_4$ in weakly acidic solutions. In moderately acidic solutions errors may be encounterd from coprecipitation. Careful addition of reagents, slow digestion of the precipitate, and use of weakly acidic solutions allows one to determine sulfate to 1% of theoretical.

Procedure

1. Weigh out ~ 1 gm samples of solidified salts to the nearest ± 0.2 mg.
2. Dissolve in 10 cc 1:1 HCl.
3. Heat solutions for 30 min at ~ 90°C, filter solids.
4. Add 10 cc 1 M $BaCl_2$ to clear solutions and digest for at least 1 hr.
5. Filter hot solutions using a Coors #3001 filtering crucible.

6. Heat precipitate at 100°C for 30 min and then at 800°C for 10 to 20 min.
7. Weigh precipitate and repeat heatings at 800°C until constant weight is achieved.
8. Calculation: $\frac{(\text{Wt } BaSO_4)(58.29)}{\text{Sample Wt}} \times 100 = \text{wt \% } M_2SO_4$

III. DETERMINATION OF TOTAL SULFUR IN ALKALI METAL CARBONATES

The analytical techniques used to determine total sulfur consists of sample oxidation using bromine in aqueous basic solutions. By using bromine in this manner quantitative oxidation can be made without evolving gaseous sulfur compounds. Based upon 10 simulated standard mixtures, the accuracy was 100.0 ± 1.2%.

Procedure

1. Weigh out ~ 1 gm salt samples to the nearest ± 0.2 mg.
2. Oxidize samples by heating for 3 min (or until sample is dissolved) in 100 ml H_2O containing 2 gm KOH, 1-2 gm CaO, and 2 ml Br_2.
3. Add 10 ml of HNO_3 slowly to evolve the residual Br_2 and then boil until the solution becomes straw yellow (about 5-10 min).
4. Add 25 ml formic acid to remove the nitrate (which badly coprecipitates with the sulfate) and boil for 10 min.
5. Add 15 ml 1:1 HCl and boil for 5 to 10 min.
6. Now add 10 ml 1 M $BaCl_2$ and allow the precipitate to digest for 1 hr.

7. Filter the hot solution in a Coors #3001 filtering crucible, heat for 30 min at 100°C and then for 10 to 20 min at 800°C.
8. Weigh the precipitate and repeat heating at 800°C until a constant weight is achieved.
9. Calculation: $\frac{(\text{Wt BaSO}_4)(58.29)}{\text{Sample Wt}} \times 100 = \text{wt \% } M_2SO_4$.

APPENDIX B. FLY ASH COMPOSITION

1. Fly ash from NCAPC, Cincinnati
2. Fly ash from Consolidation Coal Company (Mitchell Station, West Penn Power Co.).

FLY ASH COMPOSITION

Ash	Composition (wt %)								
	SiO_2	Al_2O_3	Fe_3O_4	CaO	MgO	K_2O	Na_2O	TiO_2	Other
1	43.5	18.9	14.3	2.8	1.7	1.0	0.5	1.7	5.6
2	47.1	21.5	18.0	2.6	1.4	1.4	0.5	1.2	6.3

APPENDIX C. COMPOSITIONS OF ALLOYS

The compositions of the alloys tested are given in the table.

ALLOY COMPOSITIONS (%)

Alloy	Fe	Ni	Cr	C (max)	Mn (max)	Si (max)	Co	Mo	W	Cu	Al	Other
Stainless Steel												
304	68	10	19	0.08	2	1						
304L	68	10	19	0.03	2	1						
310	51	21	25	0.25	2	1.5						
316	66	12	17	0.08	2	1						
321	68	10	18	0.08	2	1						Ti 0.4
347	67	11	18	0.08	2	1						Nb 0.8
405	87		13	0.08	1	1						
410	87		13	0.15	1	1						
430	84		16	0.12	1	1						
446	75		25	0.20	1.5	1						
1020	99											
Carpenter 20Cb3	36	34	20	0.07	2	1		2.5		3.5		Nb 1.
Multimet	85	1.5	12	0.05	1	0.5						
Nickel												
200	0.15	99.5		0.06	0.25	0.05				0.05		
201	0.15	99.5		0.02	0.2	0.05				0.05		
Inconel												
600	7	76	16	0.04	0.2	0.2						
702	0.35	79.5	16	0.04	0.05	0.2					3.4	Ti 0.7
Hastelloy												
B	5	61	1	0.05	1	1	2.5	28				V 0.4
C	5.5	54	15.5	0.08	1	1	2.5	16	3.6			V 0.35
G	20	44	22				2.5	6.5	1	2		Nb 2.0
N	5	69.5	7	0.06	0.8			17	0.6		0.5	
X	18.5	47	22		1.0	1.0	1.5	9	0.6			
Monel 400	1.0	66			1.0					31.5		
K500	1.0	65			1.0				0.5	29.5	2.8	
Tophet A		80	20									
Haynes 25	3	10	20				51.5		15			
Zircalloy II												Zr 98.5, Sn 1.5

APPENDIX D. NOMENCLATURE

A = Surface area per unit volume, ft^2/ft^3

C = Concentration of absorbate in gas, vol %

D = Diameter, ft

D_v = Diffusion coefficient, ft^2/hr

f = Friction factor, dimensionless

G_M = Molar mass velocity, lb moles/hr ft^2

h = Column height, ft

k_G = Mass transfer coefficient, lb moles/hr ft^2 atm

P_{EM} = log mean of inert gas pressure at phase boundary and in bulk of fluid

P = Total pressure, atm

R = Gas constant, ft^3 atm/lb mole °R = 0.728

Re = Reynolds number = $\frac{DV\rho}{\mu}$, dimensionless

Sc = Schmidt number = $\frac{\mu}{\rho D_v}$, dimensionless

T = Absolute temperature, °R

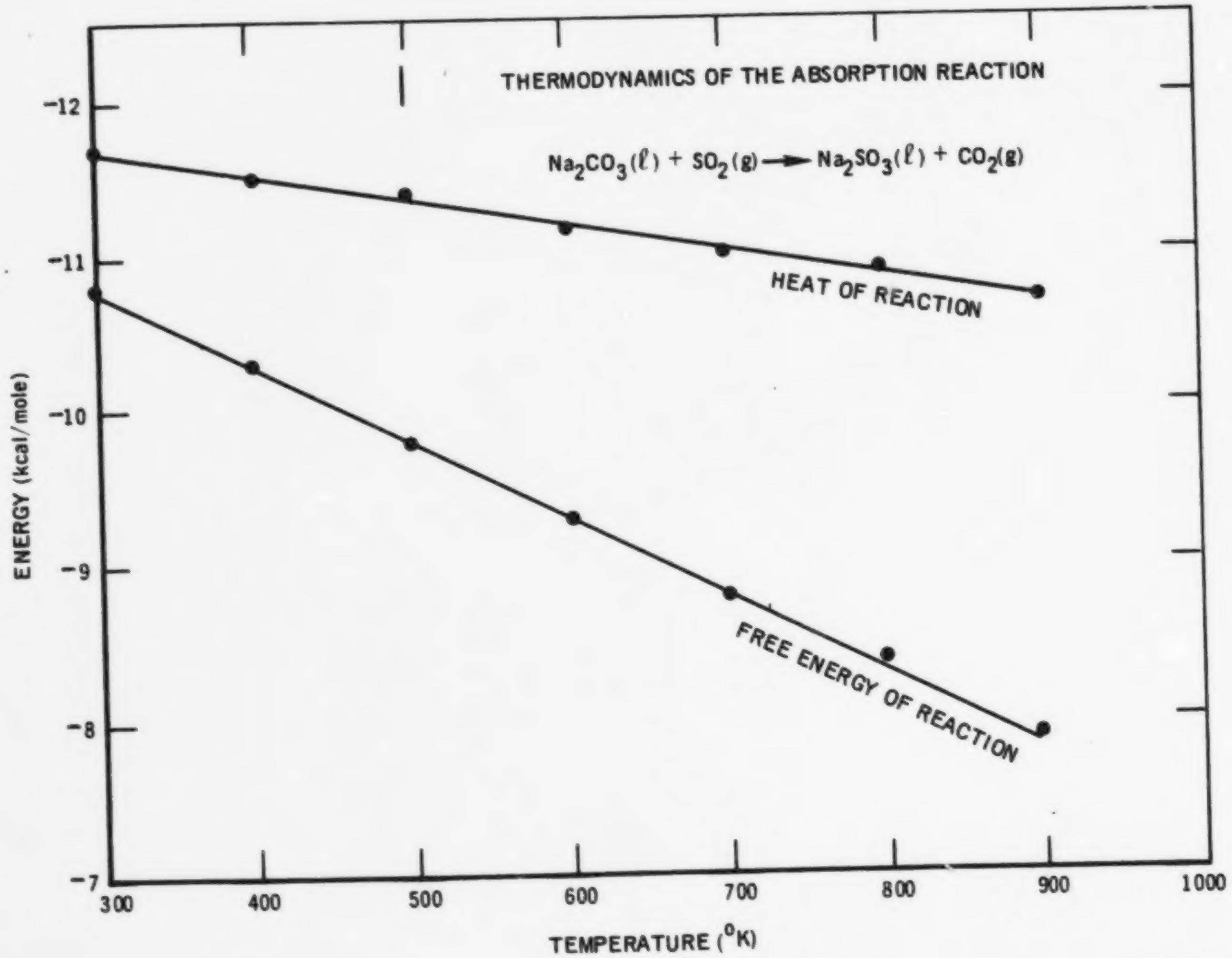
V = Velocity, ft/hr

ρ = Density, lb/ft^3

μ = Viscosity, lb/hr ft

APPENDIX E. THERMODYNAMIC DATA

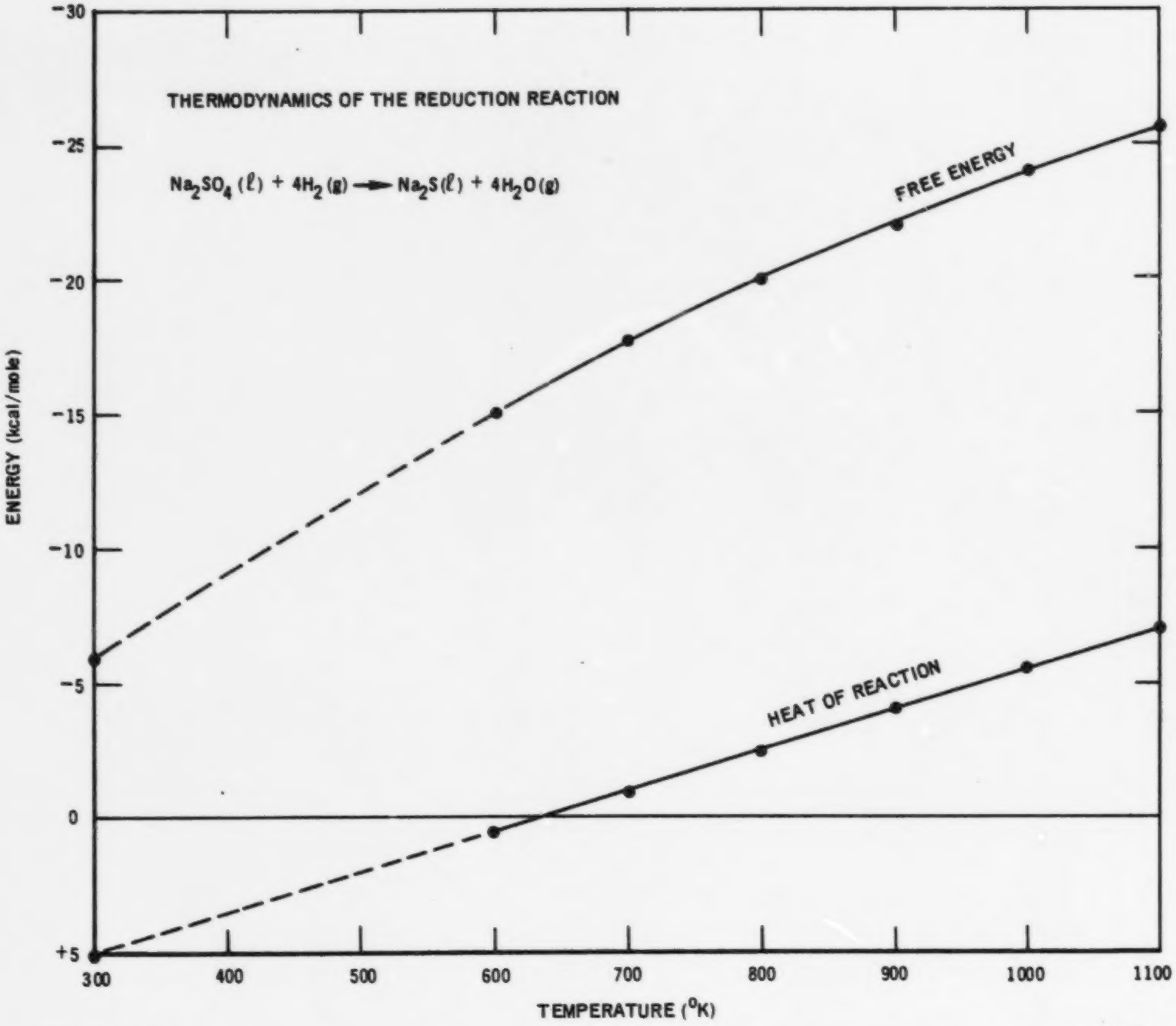
The enthalpy and free energy changes associated with the absorption, reduction, and regeneration reactions of sodium compounds are given in Figures E1, E2, and E3. Data are not available for the lithium and potassium compounds; the sodium values can be used as approximate averages for the eutectic mixture of sodium, lithium, and potassium salts.



8-12-68 UNCL

7732-4027

Figure E-1



8-12-68 UNCL

7732-4026

Figure E-2

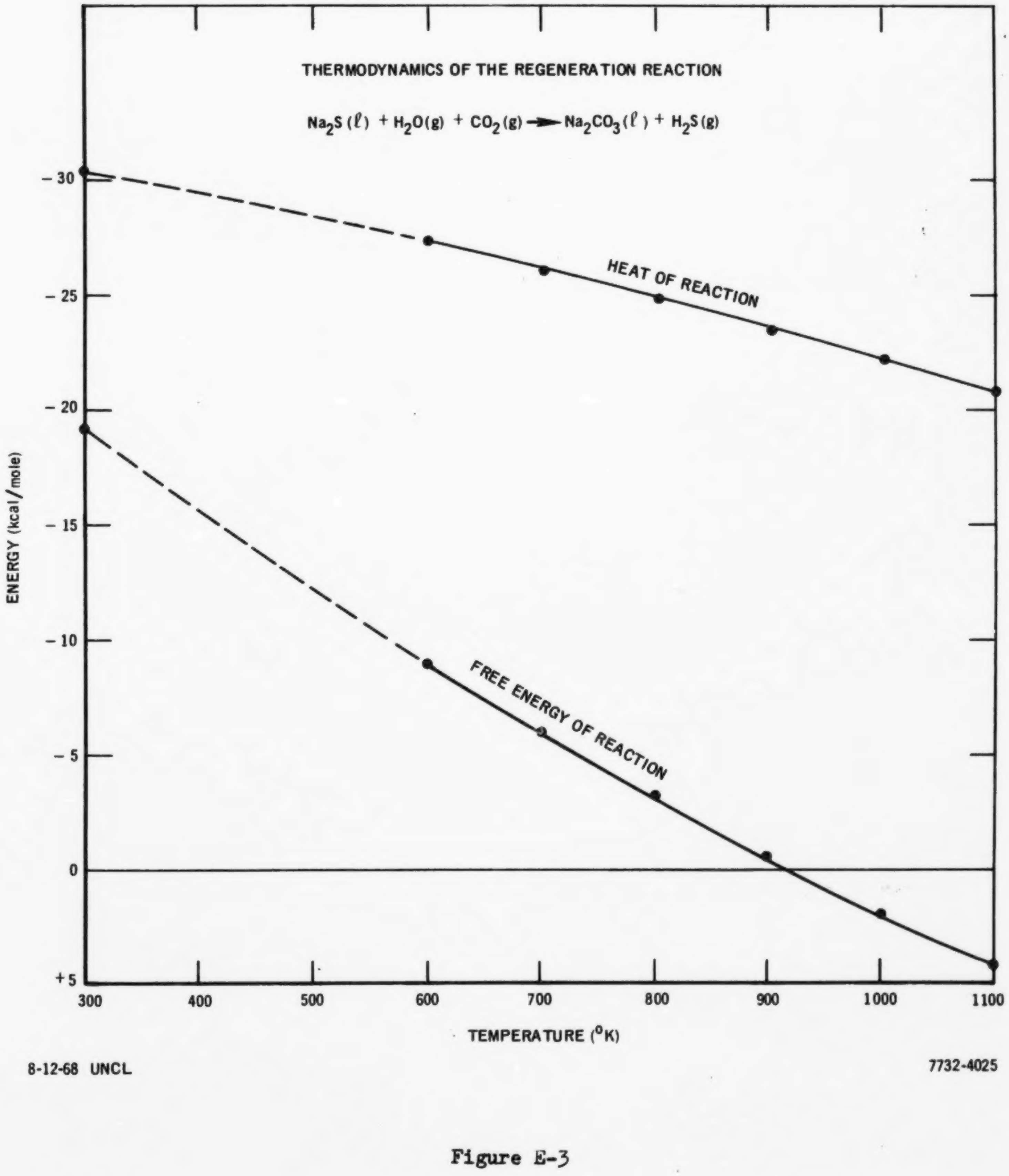

THERMODYNAMICS OF THE REGENERATION REACTION
$Na_2S(\ell) + H_2O(g) + CO_2(g) \rightarrow Na_2CO_3(\ell) + H_2S(g)$
HEAT OF REACTION
FREE ENERGY OF REACTION
ENERGY (kcal/mole)
-30
-25
-20
-15
-10
-5
0
+5
300
400
500
600
700
800
900
1000
1100
TEMPERATURE (°K)
8-12-68 UNCL
7732-4025

Figure E-3